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Mapping materials properties with Raman spectroscopy utilizing a two-dimensional detector

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Abstract

An imaging Raman system based upon a two-dimensional detector and capable of collecting simultaneously 1024 spatially resolved spectra has been constructed. Hardware and software are described which allow real-time analysis of the spectral data, leading to a large reduction in the data storage requirements. The analysis yields a one-dimensional profile (1024 points) across the sample of chemical or physical properties that are distinguishable by their Raman spectral features. Sample translations, along with repeated collection and analysis cycles, allow two-dimensional maps of chemical or physical properties to be generated rapidly. The spatial resolution and spectral precision are 5 μm and 0.16 cm⁻¹, respectively. Application to the analysis of phase transformed zones in microengineered zirconia and to measurement of an in-situ temperature profile of a single carbon fiber are presented. In a typical application, 66,560 Raman spectra from a 8 mm × 6 mm area on a partially stabilized zirconia sample were collected and analyzed in 5.4 hours to produce a two-dimensional map of the fraction of tetragonal phase transformed to monoclinic phase during crack propagation.

1 Introduction

The potential for attaining spatial resolution near the diffraction limit of light using laser Raman spectroscopy was recognized at least as early as 1973 [1]. The Raman microprobe technique makes use of a laser focused onto a sample with a microscope objective; the scattered light is collected with the same objective lens and focused onto the entrance slit of a spectrometer. The resulting Raman spectrum has a spatial resolution near 1 μm. It is possible to measure spatial variations in materials by translating the sample in one or two dimensions and collecting many single-point Raman spectra. This approach has been used to map important physical and chemical properties, for example, the residual stress in Si along a line on semiconductor device structures (where stress shifts the Raman frequency) [2][3][4][5] and the thermodynamic phase distribution in one and two dimensions across the surface of partially stabilized zirconia (PSZ) [6][7][8]. In the experiments cited the number of spectra collected and analyzed never exceeded 160, possibly due to the laborious nature of the experiments.

Obtaining Raman spectra over a large area of a sample, when a dense grid is desired, is limited severely due to time taken by sample movement, data acquisition, and data analysis. Even with multichannel detection, single-point techniques like the Raman microprobe require mechanical translation of the sample in two directions to cover the entire surface. Producing a detailed map of the chemical or physical properties of a material may require collection and analysis of tens of
thousands of spectra. Even when automated, moving the sample can take up to a few seconds per point. To map an 100×100 grid, sample translation alone would require 2.8 hours at 1 second per movement. Data acquisition and analysis times must be as fast as possible for the same reason. In addition, real time analysis of the spectra is desirable to limit data storage requirements. For example, storing the 10,000 spectra needed to produce the aforementioned 100×100 map could take up to an entire 20 MByte hard disk (binary data files at 1,000 points/spectrum × 2 bytes/point).

We have employed a two-dimensional detector to obtain Raman spectra from many spatial elements simultaneously [9][10]. We have developed an analysis technique that enables us to produce maps of a chemical or physical property of a solid sample many thousand times faster than single-point techniques. Although we have used these data collection and analyses methods only for Raman scattering, the approach is general and could be adapted to analyze data from other spectroscopic techniques which disperse light collected from a sample, e.g. photoluminescence. Raman scattered light is collected from a slit-like illuminated area on the sample and imaged onto the entrance slit of a monochromator. The dispersed light is observed with a two-dimensional position-sensitive detector. We use a microchannel plate PMT with a position-sensitive resistive anode (1024×1024 format) [11], but the method could also be implemented with a charge coupled device (CCD) detector. In this way, 1024 Raman spectra are collected simultaneously; each row of the 1024 rows in the data matrix contains the complete spectrum from one vertical position along the image of the scattered light at the entrance slit. The data matrix is analyzed to produce a one-dimensional profile of the desired chemical or physical property. Successive sample translations are used to build up a two-dimensional map of the desired property from successive one-dimensional profiles.

The data storage requirements are reduced a thousand fold by analyzing the raw data in real time and storing only the results of the analysis. We have developed and describe here a computer program which collects the spectral data from the detector, analyzes each row, stores the analysis results in a binary file, translates the sample, and repeats the process for a specified number of times. The program uses efficient and robust algorithms to compute relative intensities of different areas of the spectrum, relative compositions based on calibration spectra, or positions and linewidths of individual peaks. Data from one acquisition cycle are analyzed while the next data set is being acquired. It should be noted that the data analysis (but not data collection) requires knowing what
is to be extracted from the spectrum in advance as the spectrum itself is not saved. Thus the approach is not directly applicable to problems where it is important to save spectra for unknown future interpretation.

Spectral imaging has also been extensively developed by the space sciences community in the 1980's for mapping earth resources and for mapping objects in space such as planets or moons [12]. Instrumental concepts have evolved with detector technology [13]. The first instruments mapped a few broad spectral regions using dedicated single-channel detectors. In the "whiskbroom" imaging spectrometer approach, complete spectra (as opposed to a few broad spectral regions) from individual spatial points are collected using a linear array detector. The instrument collects data from point to point until the entire surface has been covered. The most advanced concept is the "pushbroom" approach using an area array detector to record simultaneously the spectra from a number of spatial positions. As these designs have evolved, problem areas have been identified. These include spatial and spectral resolution and steadily increasing data rates. Concerns about the quantity of data arise in spite of the fact that the data arrays employed are modest by current standards; the Airborne Imaging Spectrometer II (AIS II) uses a 64x64 (simultaneous spectral and spatial elements) format [14] and the proposed Shuttle Imaging Spectrometer Experiment (SISEX) uses three 128x128 and one 64x404 arrays covering different spectral regions [15].

An alternate approach to spatially resolved Raman spectroscopy uses Hadamard transform techniques [16]. In this approach masks are used to encode spatial information when viewing a two-dimensional region by blocking out some areas and allowing other areas to be viewed. N+1 masks are used for N spatial regions and all areas in the region are viewed approximately 1/2 of the total viewing time. The spatial information is recovered by performing a Hadamard transform on the acquired data matrix. In an elegant demonstration of mapping using Raman spectroscopy, Treado and Morris [16] coupled the Hadamard transform technique, with 128 masks for spatial resolution in one dimension, with an area array detector (CCD), yielding spatial information in the second dimension simultaneously. Incorporating a microscope they obtained a two-dimensional Raman image over a 80 μm x 80 μm region with a spectral resolution of 12 cm⁻¹. The spatial magnification was 0.6 μm/pixel; the spatial resolution as defined in this paper (Sec. 3.1) was not reported.

This paper presents results from some representative applications of the imaging technique: (1) mapping of the thermodynamic phase distribution in phase-transformed zones surrounding cracks in microengineered zirconia samples, and (2) obtaining a temperature profile along a carbon
fiber. In a typical application, the program has been used to generate a map composed of the analysis results from 66,560 Raman spectra in 5.4 hours (0.3 seconds per spectrum); the total time includes sample translation, data collection, data analysis, display, and storage of results. We estimate that performing the same experiment using a linear multichannel detector and two-dimensional sample translation would take several months; single channel detection extends the required time to many years.

2 Experimental

2.1 Data acquisition

The experimental arrangement is similar to that used for conventional Raman spectroscopy and is shown in Fig. 1. The 488 nm line of a cw Ar laser was used for all work reported here. The laser beam is expanded to a diameter of 9 mm with a telescope and focused onto the sample with a 50 mm focal length cylindrical lens, forming a slit-like illuminated area, typically 15 \( \mu \text{m} \times 3 \text{ mm} \). The Raman scattered light from the illuminated strip is then imaged onto the entrance slit (20 mm high) of the monochromator using a single lens for both scattered light collection and focusing. The distance from the sample to the entrance slit varies in the range from 400 to 800 mm. Three lenses are used in the work reported here. When high spatial resolution is desired, a 50 mm f/1.3 or a 25 mm f/1.4 camera lens is used to obtain a magnification of between 7× and 27×. To image a larger area, a 150 mm f/8 achromatic lens is used to obtain a magnification of 3.3× at a sample to slit distance of 770 mm.

After passing through a five cavity interference bandpass filter, the Raman scattered light is dispersed by a 0.64m single monochromator and collected with an imaging photon-counting PMT (1024 pixel \( \times \) 1024 pixel format), the detailed operation of which has been described previously [9] [17]. The position of each detected photon on the resistive anode is digitized as a 20 bit (10 bits for the \( x \) position and 10 bits for the \( y \) position) address which is sent to a CAMAC crate equipped with a 20-bit histogram memory controller with two-byte deep memory addresses. A full resolution image requires 2 MB of storage memory. Usually, only certain aspects of the 1024×1024 data matrix are of interest and the storage requirements can be reduced -- and the data transfer and subsequent data analysis can be speeded up -- by stripping off some of the less useful address bits. For example, in the zirconia experiments, the spectral features are broad, so the last 2 bits from the \( x \) (spectral) address are stripped off in hardware, effectively binning 4 adjacent spectral addresses, producing a 256 (spectral) by 1024 (spatial) position address which will fit in 524 kB of CAMAC memory.
The monochromator optics form a curved image of the entrance slit on the exit focal plane. As a result, spectral lines appear as curves on the detector, resulting in spectral line positions that appear to shift as a function of y (spatial) position. To correct for this effect, we apply a real-time EPROM based column correction to shift row data as it is stored in the CAMAC memory during collection.

After one data matrix has been collected and transferred to the microcomputer memory, the sample is translated by an NRC motorized positioner interfaced to the microcomputer, the CAMAC memory is cleared, and a new data acquisition cycle begins. While the CAMAC is collecting the next data matrix, the previously collected data matrix is analyzed, displayed, and stored by the computer. The real-time data analysis is discussed in Section 2.2 below.

A stored pixel represents a 25 μm × 25 μm area on the photocathode. With a 2400 groove/mm grating, the spectral dispersion is 0.4 cm⁻¹/pixel. The spatial height on the sample corresponding to one row (one Raman spectrum) in the data matrix depends on the magnification. At the highest magnification used here, 27x, one row of detector pixels corresponds to 0.9 μm on the sample. At a lower magnification (e.g. 3x) one row of pixels on the detector corresponds to 8 μm on the sample. For these two examples, the height (1024 pixels) of the imaged area on the sample is 0.9 mm or 8 mm, respectively. The width of the imaged area is the width of the slit divided by the magnification, 2 μm or 17 μm, respectively, for a 50 μm slit width. The actual spatial resolution is dependent on the quality of the imaging optical components and the opaqueness of the sample; this is discussed in Sections 3.1 and 3.5.

2.2 Real-time data analysis

The data matrix contains photon counts as a function of wavelength (x-dimension) and position (y-dimension). Each of the 1024 rows in the data matrix is the Raman spectrum for a single spatial element at the sample and can be analyzed independently from the rest of the data rows. Three methods of analyzing the data are implemented currently: method 1 compares the integrated intensity of one feature to the integrated intensity of a second feature, method 2 fits the observed spectrum to a linear combination of two previously measured calibration spectra, and method 3 determines the position, width, and intensity of up to nine spectral features by fitting them to either a Gaussian or Lorentzian line shape with a linear background term. The results of these analyses can be related to changes in sample composition -- or to a physical quantity such as temperature -- across the illuminated area to yield a spatial profile of the quantity of interest. The group of profiles
obtained by translating the sample repeatedly a specified amount in one dimension normal to the slit-like illumination yields a two-dimensional map of the chemical or physical property of interest over the surface of the sample.

Data acquisition and analysis are carried out on a 80386-based microcomputer using a computer program developed at Lawrence Berkeley Laboratory [18]. The user specifies the input parameters, such as the location of peak and background areas, at the beginning of a collection and analysis run. Some care must be taken in initial selection as only the results of the analysis and not the original data matrix are stored. Usually, a few rows summed together from a single data matrix are examined to help select the input parameters for a subsequent automated run. The program code contains extensive error trapping to avoid crashes (e.g. a divide by zero) that might cause a few hours of collected data to be lost.

With method 1, the relative fraction of one sample component with respect to a second is computed by comparing the integrated areas of their corresponding spectral features:

\[ f_1 = \frac{cI_1}{cI_1 + I_2} \]  

where \( f_1 \) is the relative fraction of component 1 in a given row, \( I_1 \) and \( I_2 \) are the integrated intensities of the two spectral features, and \( c \) is a calibration factor to account for the possibly different Raman cross sections of the two features. A schematic example of this analysis method is shown in Fig. 2. This method is useful if the sample has two components with well separated Raman features.

In method 2, Eq. (1) is used to calculate the relative fraction, with the intensities, \( I_n \), determined from a least-squares fit of the observed spectrum to a linear combination of calibration spectra. A schematic example of this analysis method is shown in Fig. 3. If pure samples are not available, the calibration spectra can be constructed from mixed samples by spectral subtraction. Standard methods are used for performing the least squares fit [19]. Although the computer program at present can analyze only a two-component mixture, it could be extended easily to analyze multicomponent mixtures without changing the mathematical method. The user selects appropriate areas of the spectrum to be fit; these are generally areas where one or the other of the components has distinctive features. Extensive error trapping is employed in the program code to avoid the
occurrence of misleading results from rows with poor S/N. For example, any return of a negative composition fraction is ignored and the corresponding point in the compositional profile is set to zero.

In method 3, up to nine spectral peaks are fit by nonlinear least-squares to either a Gaussian or Lorentzian line shape with a linear background. This method is useful for mapping a physical property that causes a Raman peak to shift or broaden, such as strain or temperature. The program uses a Levenberg-Marquardt method [20] to perform the nonlinear least-squares fit. High spectral precision can be achieved by measuring the spectral line of interest in the sample relative to a Ne calibration line for each row in the data matrix. The calibration method is discussed and demonstrated in Section 3.2. Using Ne calibration, line positions are measured with a precision of ±0.50 cm⁻¹ over the full height of the imaged area and 0.16 cm⁻¹ over shorter distances using a 2400 groove/mm grating.

To collect and analyze data efficiently, one wants the data analysis time to be equal to, or less than, the typical 300 s collection time, so that collection of the next data set can take place simultaneously with analysis of the current data set. Method 1 is the fastest analysis method and 2.5 s are required with a 25 MHz 80386/80387 based microcomputer to ratio two moderately broad spectral features (150 spectral data points, 900 rows). Method 2 is slower since it involves a matrix inversion and 63 s are required for the same data set. Since method 3 uses an iterative procedure it requires the longest time; fitting of two spectral features takes 820 s for 700 rows (700 spectra) [21].

3 Results and Discussion

3.1 Spatial resolution

The effective spatial resolution of the imaging spectrometer system is a function of the magnification of the collection optics, the modulation transfer function (MTF) of the collection optics and the spectrometer combination, and the detector area corresponding to a pixel (25 μm × 25 μm). Spatial resolution is measured using a source with alternating light and dark bars and is defined as the bar spacing at which the contrast, \((I_{\text{max}}-I_{\text{min}})/(I_{\text{max}}+I_{\text{min}})\) [22], drops below 0.1. In any digital imaging system more than two pixels are required to provide contrast; starting at a bright bar, one pixel for a dark region and one pixel for the next bright bar. For example, at 27×, the highest magnification used in this work, the sample is imaged onto the y-dimension of the detector at 0.9 μm/pixel and the limiting spatial resolution is 1.8 μm.
The effective spatial resolution was measured using a USAF 1951 test target. The negative test target was backlit with a flashlight. The target consists of a pattern of bars that systematically decrease in width and spacing. Group 7, the most closely spaced group, has elements that contain bars with spacings from 7.8 to 4.4 μm. In separate experiments, the test target was imaged onto the entrance slit of the monochromator with the 25 mm (27×) and 50 mm (13×) lenses. The resulting spectral image as viewed on an oscilloscope or the graphics monitor (see Fig. 1) is a series of vertically spaced horizontal bars. The intensity as a function of y-position is obtained by summing 30 x-pixels in each row; 30 x-pixels corresponds to a typical region used to fit a narrow spectral line with method 3. The measured intensity as a function of distance at the test target is shown in Figs. 4a and 4b for the 27× and 13× magnifications, respectively. In Fig. 5a the measured contrast for both lenses is plotted as a function of the modulation in line pairs/mm (lp/mm). The 25 mm lens results in higher contrast at all modulations, although it is not twice that of the 50 mm lens. The effective spatial resolution at 13× magnification is 7 μm, which may be compared with the 4 μm limit set by the area of the detector pixels. We can conclude that the optical aberrations in the monochromator do not limit the spatial resolution markedly. The effective spatial resolution at 27× magnification, 5 μm, is significantly larger than the 1.8 μm limit set by the area of the detector pixels. In this case the optical MTF of the lens limits the effective spatial resolution.

The monochromator forms a curved image of the entrance slit on the exit focal plane which may affect the spatial resolution towards the top and bottom of the entrance slit. In addition, the MTF of the collection lenses decreases away from the optical axis due to off-axis aberrations and this may affect the spatial resolution when imaging the sample onto the top and bottom of the entrance slit. The contrast for modulations of 70.8, 90.5, and 114 lp/mm was measured for both lenses as a function of position along the entrance slit by moving the sample vertically. The results are shown in Fig. 5b. For the 25 mm lens, the measured contrast did not change within the experimental error; however, for the 50 mm lens the contrast drops off towards the top and bottom of the image. The overall spatial resolution of the Raman imaging system is 5 μm over 600 pixels (i.e. over 540 μm) with the 25 mm lens and 7 μm over 400 pixels (i.e. over 760 μm) with the 50 mm lens.
3.2 Spectral precision

The monochromator optics cause spectral lines to appear as curves on the detector resulting in spectral line positions that appear to shift as a function of spatial position. This is partially corrected by the EPROM correction described in the experimental section, but since this correction is applied to the digital data, it is limited to a precision of one pixel.

In Fig. 6a, we show the results of an experiment in which the spectral position of a Ne calibration line was determined as a function of position on the entrance slit. Images were collected and analyzed with (upper trace) and without (lower trace) the EPROM based slit correction. The apparent shift of the Ne line position is seen in the lower trace and the small steps from the digital slit correction are seen in the upper trace. The precision of the line position determination is clearly better than one pixel. Therefore, to obtain a higher spectral precision across the full height of the entrance slit than can be obtained with the hardware slit correction alone, a spectral calibration along the spatial dimension is required. The calibration spectral image is acquired either at the same time or after the sample spectral image is obtained. However, the curvature of the image of the entrance slit on the detector is not uniform across the x-dimension, i.e., the amount of curvature in the y-dimension is a function of the x- or spectral position. Therefore, for the highest precision, the calibration spectral image is acquired after the monochromator is slewed such that the calibration line position in the central row of the image occurs at nearly the same position as the corresponding sample line position of interest. Relative line positions in the sample spectra are then determined from the differences between the sample and calibration line positions in each row.

We measured the spectral precision by imaging the (111) surface of a single crystal Si sample that was believed to be uniform and stress-free. Method 3 was used to determine the peak center (Lorentzian lineshape) for 900 spatially resolved spectra from a 1.8 mm illuminated strip on the sample. A Ne calibration spectral image was then collected after slewing the monochromator, as discussed above. Figure 6b shows the relative shift of the Si Raman line at ca. 520 cm$^{-1}$ compared to the Ne line. The spectral precision is ±0.5 cm$^{-1}$ across the entire imaged region or less than one pixel. The spectral precision in a small spatial region is much higher as can be seen by examining the local variation in the Raman frequency which is about ±0.1 cm$^{-1}$ or 0.2 pixels. As a result, the change in Raman frequency arising from a discontinuous spatial feature, such as the edge of a component on a circuit board, can be measured with a higher precision than a more slowly varying feature. The spatial and spectral performance of the instrument are summarized in Table 1.
3.3 MgO-PSZ calibration samples

Crack growth in inherently brittle ceramic materials can be slowed or arrested by the formation of a phase-transformed zone surrounding the crack and crack tip. Such transformation toughening has been widely studied; zirconia is a model material. In pure zirconia, the martensitic phase transition from the tetragonal phase to the monoclinic phase occurs at about 1100 K; however, additives such as MgO, CeO$_2$, Y$_2$O$_3$, and Al$_2$O$_3$ can stabilize the tetragonal phase at room temperature. These materials are called partially stabilized zirconia (PSZ) if there is some monoclinic phase in the sample at room temperature and tetragonal zirconia phase (TZP) if the tetragonal phase is totally stabilized and there is no monoclinic phase in the sample. In the stabilized materials, the martensitic phase transition from the metastable tetragonal to the monoclinic phase occurs in the high stress fields in the vicinity of a propagating crack tip. The transformed zone so produced shields the crack tip from the applied stress, such that a higher applied stress is required for additional crack propagation and the material is toughened. The degree of toughening is related to the spatial extent and the amount of transformation of the transformed zone. Cyclically induced fatigue crack growth has also been observed in these phase-stabilized zirconias [23]. For a complete understanding of these materials, a quantitative measure of the extent of transformation (spatial and amount) is required. The exact toughening mechanism in PSZ and TZP is an active area of materials research and we have given a simplified picture here; Evans [24] has recently reviewed toughening in ceramics.

Several methods have been used to study transformed zones in stabilized zirconias. Nomarski photography [25] provides a visualization of the size and shape of the transformed zone but not the amount of transformation. X-ray diffraction (XRD) is quantitative [8] [26] but has been shown to be nonlinear with composition [27] and achieves only modest spatial resolution, $\sim$100 μm. Raman microprobe methods are quantitative and have good spatial resolution, $\sim$1 μm [6] [28] [29]. However, XRD and Raman microprobe have the disadvantage of being single point measurements and it is prohibitively time-consuming to map the zirconia phase composition in the vicinity of a crack tip using these techniques.

A series of MgO-PSZ calibration samples were provided for us by Rockwell International with relative fractions of monoclinic phase, $F_{\text{mono}}$ (defined below), varying from 1.0 to 0.1. The monoclinic and tetragonal phases of these samples total about 45% of the volume fraction; the balance of the material is cubic zirconia (which does not exhibit a Raman spectrum) and MgO. Researchers at Rockwell determined the phase composition of the samples by XRD and Raman
microprobe [8]. XRD measures the volume fraction of the three zirconia phase components, cubic, monoclinic, and tetragonal. Since cubic zirconia does not have a Raman spectrum, Raman spectroscopy can only measure the relative fractions of the monoclinic and tetragonal phases. Our nomenclature is as follows: \( f_m, f_t, \) and \( f_c \) are the volume fractions of the three zirconia phases and \( F_{\text{mono}} = f_m/(f_m + f_t) \) is the relative monoclinic fraction of the Raman active species.

Raman images were collected from each of the Rockwell calibration samples under 3.3x magnification. The images were analyzed using method 2 with the reference spectra (Figs. 3a and 3b) being those of the pure tetragonal and pure monoclinic phases, respectively. We assumed \( c = 1 \) in Eq. (1), which is equivalent to assuming that the monoclinic and tetragonal phases have identical Raman cross sections. This appears to be a reasonable assumption, considering the small (3%) volume difference between the two phases. The resulting profiles are shown in Fig. 7. The relative monoclinic phase, \( F_{\text{mono}} \), ranges from 0.10 to 1.00 and is constant across all the samples. Profiles were also measured using method 1 by computing the ratio of the area under the peaks at 264 cm\(^{-1}\) (tetragonal) and at 181 and 192 cm\(^{-1}\) (monoclinic); these results are in very good agreement with the results of analysis by method 2 and there are no systematic differences.

Table 2 summarizes results from the XRD and Raman microprobe measurements of Marshall et al. [8] and the imaging Raman results of this work. The Rockwell values of \( F_{\text{mono}} \) were determined from a Raman microprobe measurement by computing the ratio of the integrated peak intensities at 181 cm\(^{-1}\) (monoclinic) and 145 cm\(^{-1}\) (tetragonal), similar to our method 1 analysis. Figure 8 compares the two Raman measurements; agreement is good, except at low values of \( F_{\text{mono}} \) where the Rockwell measurement is consistently higher. Also plotted are the XRD results \( (f_m) \) from Table 2. The XRD results appear linearly correlated, with a positive intercept. Marshall et al. saw similar behavior when they compared their XRD and Raman results and their interpretation was that the Raman measurement was nonlinear in monoclinic volume fraction. However, other work [27] suggests that the XRD measurement may be nonlinear. In zirconia XRD the tetragonal and cubic peaks are not resolved and nonlinear calibration curves due to differences in the reflecting power of the three phases have been reported [30]. In any case, the differences between the methods are not large enough to affect significantly the measurements of transformations produced by crack growth; increases in \( F_{\text{mono}} \) are typically about 10%.

3.4 MgO-PSZ transformed zones

The imaging techniques described in this paper have been used to obtain maps of the transformed zones of MgO-PSZ samples with carefully grown cracks[31]. We summarize here
The details of the crack growth method and cyclic-fatigue studies have been reported elsewhere [23] and only a brief summary will be given here. Cracks were produced in 3 mm thick specimens using 50 Hz sin wave cyclic loading with a load ratio $R = 0.1$ where $R = K_{\text{max}}/K_{\text{min}}$; $K$ is the applied stress. The cyclic stress-intensity is $\Delta K = K_{\text{max}} - K_{\text{min}}$. In one specimen, a block loading change from $\Delta K = 9.5$ to $\Delta K = 8.5$ MPa$\sqrt{m}$ was followed by a single-cycle overload $K_{\text{max}} = 12.3$ MPa$\sqrt{m}$. In a second specimen, a crack was grown with cyclic loading to a crack extension of 3.7 mm followed by an $R$-curve test in which a constant crack tip velocity is maintained by applying a steadily increasing (non-cyclic) load. The resulting maps, shown in Fig. 9, were obtained under $3.3\times$ magnification and each is obtained from the analysis of 66,560 Raman spectra. The shape of the transformed zone in the vicinity of the crack tip is clearly shown. The shape of the zone behind the crack tip retains the stress history of the sample as shown by the differences in the transformed zones in Figs. 9a and 9b and by the large zone associated with the single-cycle overload in Fig. 9a. The increasing loads necessary to maintain a constant crack tip velocity result in increasing zone sizes, Fig 9b. The extent of shielding at the crack tip by the transformed zone can be modeled and used to predict the crack-growth rate from the observed extent of the transformed zone [31].

The crack-induced transformed zone measured for MgO-PSZ in this work can be compared to the results of other studies. Marshall et al. [8] measured the maximum transformation with Raman microprobe and XRD and also the width of the zone with Nomarski microscopy, for the same MgO-PSZ samples we used. The maximum transformation observed for a variety of samples was 22%, in reasonable agreement with our value of about 18%. The zone widths as observed by Nomarski photography were ca. 1.5 mm, in good agreement with our values. Early theories assumed that the tetragonal to monoclinic transformation would be 100% in the area around the crack tip. In contrast, no quantitative measurement has shown a transformation greater than about 60%.

3.5 CeO$_2$-TZP transformed zone

In contrast to the MgO stabilized zirconias discussed above, stress-free samples of CeO$_2$ stabilized zirconia (CeO$_2$-TZP) have no monoclinic phase present at room temperature. Transformation toughening occurs in TZP samples, but the degree of transformation and the width of the transformed zone are much smaller than in PSZ. These factors make the quantitative analysis of transformed zones in TZP more difficult. Figure 10 shows a spectrum of CeO$_2$-TZP in the vicinity of a crack and a spectrum obtained from the same CeO$_2$-TZP sample in a region far away from the crack. The monoclinic peaks in the spectrum from the crack region are tiny, but visible. To analyze
the spectrum using method 2, the pure tetragonal and pure monoclinic spectrum are required. Since the pure tetragonal and monoclinic zirconia spectra in CeO$_2$-TZP are slightly different than those of MgO-PSZ (peaks are shifted and in different ratios), the calibration spectra in Fig. 3 could not be used. Instead, a spectrum obtained far from the crack where there was no transformation was used as the pure tetragonal spectrum. The monoclinic calibration spectrum was then constructed by subtracting the tetragonal spectrum from the spectrum with the small amount of monoclinic phase obtained at the crack. The result is a suitable, albeit noisy, pure monoclinic spectrum. A profile of a line across the crack tip was collected for 2.5 hours under 13x magnification and the resulting profile of the transformed zone (method 2 analysis) is shown in Fig. 11. A typical MgO-PSZ profile is also shown in Fig. 11 for comparison. The 2% maximum transformation measured in CeO$_2$-TZP is much smaller than that found in the MgO-PSZ sample. The CeO$_2$-TZP zone is also very narrow, about 230 \( \mu \text{m} \) FWHM. In spite of the small size of the zone, the precision of the data analysis is very good. By examining the variation in the monoclinic fraction in the profile, \( F_{\text{mono}} \) is estimated to be measured with a precision of \( \pm 0.2\% \) for this data set.

A transformed zone could not be seen with Nomarski interference microscopy from the CeO$_2$-TZP sample used in this work [32]. This implies that the transformed zone is very narrow and/or the amount of transformation is small. A Nomarski study [33] of crack induced transformations in CeO$_2$-TZP samples similar to those used in our study found a 40 \( \mu \text{m} \) wide transformed zone, consistent with the narrow zone observed here.

Since the CeO$_2$-TZP zone is very narrow, we must consider the limiting effects of sample transparency. The spatial resolution of the instrument is sufficient to measure zone widths on the order of 5 \( \mu \text{m} \) in an opaque sample (section 3.1). In opaque samples, the scattered light flux from a given area on the sample arises from a small volume given by the area and the optical skin depth. However, in a translucent sample, the scattered light flux from a given area on the sample arises from a much larger volume. The cross-sectional area of this volume increases with increasing depth, leading to a smearing out of the spatial information and a reduction in the spatial resolution. To estimate this effect we collected an image from the edge of the sample and observed the total scattered intensity as a function of position across the edge. The edge of the sample appeared to have a "width" of 31 \( \mu \text{m} \), which is approximately four times larger than the limiting spatial resolution and is due to the translucency of the sample. The effective spatial resolution (31 \( \mu \text{m} \)) in the
translucent CeO₂-TZP is still a factor of four less than the observed transformed zone half-width (115 μm) and we conclude that sample translucency does not cause a significant broadening of the observed zone.

3.6 In-situ temperature profile of single carbon fiber

To illustrate the mapping of a physical property of a material we present a measured in-situ temperature profile of a single carbon fiber. In the characterization of single carbon fibers (diameter ≈ 8 μm) by Raman spectroscopy a laser beam is focused onto the fiber. Quite low laser powers, on the order of 10 mW, coupled into the small sample volume result in significant heating of the sample, which produces changes in the observed Raman spectrum. This work was part of an investigation [34] of the chemical and physical changes produced by laser heating in the Raman characterization of carbon fibers and only the experimental details relevant to Raman imaging will be given here.

The Raman spectra of carbon fibers are dominated by a peak near 1580 cm⁻¹ associated with crystalline graphite (G-band), and a peak near 1380 cm⁻¹ associated with disordered graphite (D-band) [35]. Even at low laser powers it is observed that the positions of both peaks shift to lower frequency with increasing laser power due to heating of the fiber by the laser. In a separate experiment with bulk graphite we measured the temperature dependence of the G-band position to be 0.040 cm⁻¹/K. When this is combined with our measured spectral resolution of 0.5 cm⁻¹, we anticipate being able to determine the temperature of individual spatial elements on a carbon fiber with a precision of 12 K.

The following experiment was performed. A 2 mm diameter 488 nm laser beam (probe) was focused with a cylindrical lens along a vertically-mounted single 8 μm diam fiber and the Raman scattered light from a 1.6 mm length of the fiber was collected and focused onto the entrance slit of the spectrometer. The magnification was 12.5× and the collection time was 10 minutes. The probe laser shifts the G-band position about 4 cm⁻¹ from that of the unheated fiber and the observed frequency as a function of vertical position along the fiber is constant as shown in Fig. 12a. A second 488 nm laser beam (heating) was then focused with a spherical lens to a 100 μm spot in the center of the imaged area. The observed profile of the G-band position when the sample is illuminated with both the probe and heating lasers is also shown in Fig. 12a. The heating laser causes the G-band to shift 20 cm⁻¹ to lower frequency in the center of the imaged area. The measured temperature dependence of the G-band in bulk graphite can be used to convert the Raman frequencies to temperature and this is done in Fig. 12b. The maximum temperature produced by the heating
laser is 650°C and the temperature distribution has a FWHM of about 500 μm. The solid line in Fig. 12b is a fit to a heat transfer model [34] using free convective cooling with the absorbed laser power and fiber thermal conductivity as variable parameters. The excellent agreement (and reasonable values of the parameters [34]) confirms that the observed frequency shifts in the fibers are due to laser heating.

4 Conclusions

Spatially resolved Raman spectroscopy is a promising quantitative and non-destructive technique for studying advanced materials. The spatial resolution (5 μm) approaches that of the Raman microprobe (1 μm), while multiplexed two-dimensional detection and real-time data analysis allow one-dimensional profiles and two-dimensional maps to be generated orders of magnitude faster.

In calibration experiments with MgO-PSZ samples, multiplexed spatially resolved Raman yields results in good agreement with the Raman microprobe in measuring the monoclinic fraction. Both Raman techniques are in fair agreement with X-ray diffraction measurements. Raman mapping of phase transformations accompanying cyclic-fatigue crack growth in PSZ has revealed zone sizes ranging from 230 to 1500 μm and amounts of transformations ranging from 0.2% to 20%. The maps result from acquisition and analyses of 66,560 Raman spectra in less than six hours. The sensitivity of the technique is shown in the first quantitative measurement of the transformation zone in a CeO₂-TZP. The small amount (ca. 2%) and extent (230 μm) of the transformed zone would make this analysis very challenging with any other technique.

The speed at which analyses can be performed makes possible experiments that would not have been considered previously. For example, forces can be applied to a PSZ sample to create a crack growth rate of ca. 1 mm every 10 minutes. With our current detector/computer combination we can process about 10 profiles in this time using method 2, just enough to construct a reasonable map of the transformed zone. Repeated sweeps of the area in front of the propagating crack tip would produce real-time imaging of the phase transformations as the crack propagates. With currently available software and hardware (32 bit compiler, special co-processor) and a CCD detector capable of higher count rates we estimate that the cycle time for a single profile could be reduced to about 10 s. Other possible real-time applications of Raman imaging include epitaxial growth of semiconductor layers and superlattices.
5 Acknowledgments

We thank R. Dauskardt and R. Ritchie of the LBL Center for Advanced Materials for suggesting the Raman analysis of PSZ and for providing the samples. This work was supported by the Director, Office of Energy Research, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.
Table 1. Performance of imaging Raman spectroscopy apparatus.

<table>
<thead>
<tr>
<th>Spacial (for 27x magnification)</th>
<th></th>
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<tbody>
<tr>
<td>size of detector pixels on sample</td>
<td>0.9 μm/pixel</td>
</tr>
<tr>
<td>imaged area height</td>
<td>0.7 mm</td>
</tr>
<tr>
<td>resolution</td>
<td>5 μm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spectral (with 2400 groove/mm grating)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>range</td>
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</tr>
<tr>
<td>dispersion</td>
<td>0.4 cm(^{-1}) / pixel</td>
</tr>
<tr>
<td>bandwidth</td>
<td>400 cm(^{-1})</td>
</tr>
<tr>
<td>resolution</td>
<td>1.2 cm(^{-1})</td>
</tr>
<tr>
<td>precision (local)</td>
<td>0.16 cm(^{-1})</td>
</tr>
<tr>
<td>precision (over entire image)</td>
<td>0.50 cm(^{-1})</td>
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</table>
Table 2. Comparison of x-ray diffraction and Raman measurements of the relative monoclinic fraction in MgO-PSZ calibration samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>X-ray diffraction</th>
<th>Raman microprobe</th>
<th>Raman this work</th>
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<tr>
<td></td>
<td>Rockwell (a)</td>
<td>Rockwell</td>
<td></td>
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<tr>
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<td>0.10</td>
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<td>0.12</td>
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<tr>
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<td>0.35</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
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<tr>
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<td>0.88</td>
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<tr>
<td>24</td>
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<td>0.94</td>
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</tbody>
</table>

a) The measured monoclinic volume fraction from the XRD measurements was converted to relative monoclinic fraction, $F_{\text{mono}}$, assuming $f_c = 0.55$ [8].
References

11. ITT F4146M position sensing photomultiplier with Surface Science Labs 2401 position computer.
19. The NAG Fortran PC50 Library Handbook, Numerical Algorithms Group Ltd, 1983. (See Simultaneous Linear Equations routine F04JGF for solution of the minimal least squares problem, Ax=b, where b contains the overdetermined spectral data, A contains the "pure" spectra, and x contains the two composition multiples.)
21. This figure is for the computer running in 16 bit real mode. We anticipate a factor of two increase in computing speed when we convert our data analysis program to operate in 32 bit protected mode.
32. R. Dauskardt, Lawrence Berkeley Laboratory, private communication.


Figures

Fig. 1. Experimental configuration of the imaging Raman instrument. The 488.0 nm laser line is focused on the sample by a 50 mm focal length cylindrical lens and the scattered light is collected by a multi-element, high-quality lens; a 50 mm focal length camera lens is shown. The inset illustrates the sample translation used to acquire multiple one-dimensional profiles for building up two-dimensional maps.

Fig. 2. Analysis of a Raman spectrum using Method 1. The ratio of the integrated areas of regions 3 and 6 determine the relative fraction of a component of a mixture; points 1, 2, 4, and 5 are used as endpoints for background subtraction. The spectrum is that of a partially stabilized zirconia.

Fig. 3. Analysis of a Raman spectrum from partially stabilized zirconia (PSZ) using Method 2. a) Pure tetragonal calibration spectrum and b) pure monoclinic spectrum. c) The observed PSZ spectrum and a spectrum calculated from the results of a least-squares fit, with $F_{\text{mono}} = 0.15$, using the pure spectra in (a) and (b). The upper trace in (c) shows the residuals from the least squares fit, offset and multiplied by a factor of 3.

Fig. 4. The spatial resolution of the imaging Raman instrument is measured with a USAF 1951 test target. a) Spatial intensity profile of group 7 of the test target imaged on the entrance slit using a 25 mm focal length collection lens to obtain 27× magnification. b) Spatial intensity profile of group 7 using a 50 mm focal length collection lens to obtain 13× magnification. The spacing between bars in the various elements on the test target is indicated (μm).

Fig. 5. The spatial resolution is defined as the spatial frequency when the contrast between bars on the test target drops below 0.1. a) The measured contrast in the elements of group 7 from Figs. 4a and 4b is plotted as a function of spatial frequency in units of line pairs/mm (lp/mm): (circles), 25 mm lens; (squares), 50 mm lens. b) The measured contrast of two elements from group 6 is plotted as a function of vertical position at the detector; the center of the detector is at 500 pixels. The open circles show the 72 lp/mm element imaged with the 25 mm lens; the open triangles show the 114 lp/mm element imaged with the 25 mm lens; and the closed triangles show the 114 lp/mm element imaged with the 50 mm lens.

Fig. 6. Spectral precision of the imaging Raman instrument. a) Ne line position as a function of vertical position at the detector; upper trace with EPROM slit correction and lower
trace without slit correction. b) Measured frequency of the Si Raman line at ca. 520 cm\(^{-1}\) relative to a Ne calibration line as a function of position across the specimen; one spectral pixel is 0.4 cm\(^{-1}\).

Fig. 7. Profiles of the relative fraction of monoclinic phase, \(F_{\text{mono}}\), of seven Rockwell MgO stabilized zirconia calibration samples. The profiles indicate that the calibration samples are homogeneous.

Fig. 8. Comparison of the relative monoclinic fraction, \(F_{\text{mono}}\), in MgO stabilized zirconia determined by this work with measurements on the same samples made at Rockwell by Raman microprobe (circles) and x-ray diffraction (triangles). Measurements that agree exactly would lie on the line.

Fig. 9. Maps of the monoclinic fraction, \(F_{\text{mono}}\), in phase transformed zones surrounding cracks grown in MgO stabilized zirconia. a) Map of the transformed zone surrounding a crack grown by cyclic stress with a single cycle overload. b) Map of the transformed zone surrounding a crack grown by cyclic stress followed by a steadily increasing non-cyclic load (R-curve test; see text). Each map comprises the analysis results of 66,560 Raman spectra.

Fig. 10. Raman spectra of CeO\(_2\) stabilized zirconia. The lower trace shows the Raman spectrum away from the crack; no monoclinic phase is observed. The upper trace shows the Raman spectrum in the vicinity of the crack tip; small monoclinic peaks are observed near 180 and 380 cm\(^{-1}\).

Fig. 11. Profiles of the monoclinic fraction, \(F_{\text{mono}}\), across crack tips in microengineered zirconias having varying degrees of fracture toughness. Upper graph: MgO stabilized zirconia with 22% maximum transformation and a zone width (FWHM) of 1 mm with a fracture toughness of 16 MPa\(\sqrt{m}\). Lower graph: CeO\(_2\) stabilized zirconia with 2% maximum transformation and a zone width (FWHM) of 230 \(\mu\)m with a fracture toughness of 9.5 MPa\(\sqrt{m}\).

Fig. 12. The temperature of small volume elements along a carbon fiber is determined in a pump-probe experiment. a) G-band frequency as a function of position along a carbon fiber for the probe laser only (closed circles) and for both the probe and heating lasers (open squares). b) The fiber temperature as a function of position along the fiber with the probe and heating lasers; the temperature is calculated from the temperature dependence of the Raman shift measured for bulk graphite. The line is a fit to a convective heat transfer model.
Ar+ laser, 488 nm

50 mm lens

Sample

50 mm f/1.3 multi-element camera lens

Entrance slit

Interference filter

0.64 m single monochromator

Imaging PMT (Resistive anode)

Position computer
10 bit A/D
1024x1024

Analog

Digital

CAMAC CRATE
Histogrammer and memory

25 MHz 386/387 EGA Monitor
1024x1024 Color graphics monitor

Scope

Fig. 1
Fig. 3
Fig. 4a

(a)

1 pixel = 0.9 \( \mu \text{m} \)
Fig. 4b

(b)

1 pixel = 1.8 μm
Fig. 5a
Fig. 6a
Fig. 6b
Fig. 8

Rockwell x-ray and Raman microprobe vs LBL Raman
Fig. 10
Fig. 12a

- Probe laser
- Probe + heating lasers
Fig. 1zb

---Laminar free convection

Temperature (°C)

Position (µm)