

Quantitative Raman spectroscopy of Mg–(PSZ) ceramics

G. L. KELLY, T. R. FINLAYSON

Department of Physics, Monash University, Clayton, Victoria, 3168, Australia

E-mail: t.r. finlayson@sci.monash.edu.au

Micro-Raman spectra were collected from an MS (maximum strength) grade Mg–PSZ sample. Both the Mg–PSZ sample and the laser polarization were rotated and the resulting spectra examined. Quantitative analyses of these spectra showed significant variation arising from the effect of grain orientation with respect to the laser polarization direction. The minimum collection volume necessary for reproducible spectra was assessed.

© 1998 Kluwer Academic Publishers

1. Introduction

Magnesia–partially stabilized zirconia (Mg–PSZ) has a microstructure consisting of cubic grains with lenticular precipitates. These precipitates may be tetragonal, monoclinic or orthorhombic phase depending on the processing and mechanical history of the material. The improved toughness of this ceramic may be largely attributed to the stress-induced, tetragonal–monoclinic phase transformation. Hence there is much interest in monitoring this phase transformation.

Raman spectroscopy is commonly used to quantify the amounts of monoclinic and tetragonal phases present on zirconia ceramics [1–7]. Early work found that the Raman spectrum of monoclinic zirconia was dependent on the crystallographic orientation of the sample with respect to the polarization of the incident light [8]. Most quantitative analyses of the spectra are based on the method described by Clarke and Adar [1]. This method attempts to counter any orientation effects by including two peaks corresponding to each of the tetragonal and monoclinic phases in the analysis.

2. Method

Micro-Raman spectra were collected using a Dilor spectrometer incorporating confocal optics. These enabled data to be collected from a volume between 1 and 8 μm^3 . The 514 nm line of an argon laser provided illumination at an intensity of 25–50 mW at the sample surface. Data were collected over wavelengths corresponding to Raman shifts in the range 90–690 cm^{-1} . Collection times were adjusted to give a peak height of at least 1000 counts for the most intense peak in the spectrum.

The material used was MS (maximum strength) grade Mg–PSZ supplied by ICI Australia Operations Pty. Ltd. The surface of the sample was polished by hand using successively finer grades of silicon carbide paper. The final polish was obtained with 3 μm dia-

mond paste on a cloth disc on an automatic polisher for 2 h. The surface was then etched in concentrated hydrofluoric acid (HF) for 3 min to reveal the grain boundaries. Micro-Raman spectra were taken from various grains to confirm grain–grain variation in the spectra obtained. The laser was then focused on to a single grain. Spectra were obtained with both horizontal and vertical polarization of the laser. The sample was then rotated 90° and the experiment repeated.

The preparation of the polished cross-section inevitably resulted in some transformation near the surface. The influence of this transformation on the measured spectrum could be minimized by utilizing the confocal optics available on the Dilor spectrometer, to collect data from a scattering volume 6–8 μm under the surface.

The analysis method used to quantify the relative amounts of monoclinic and tetragonal phases present in the Mg–PSZ samples was based on that described by Clarke and Adar [1]. The peaks at Raman shifts of 145 and 265 cm^{-1} arising from the tetragonal phase, and those at 180 and 190 cm^{-1} from the monoclinic phase, were used to quantify the spectra. These peaks were fitted with Lorentzians and the background subtracted. The integrated intensities (I_{180} , I_{190} , I_{145} and I_{265}) were then used in Equations 1 and 2, where F_m and F_t are the relative amounts of the monoclinic and tetragonal phases respectively, $I_m = I_{180} + I_{190}$ and $I_t = I_{145} + I_{265}$

$$F_m = \frac{I_m}{I_m + I_t} \quad (1)$$

and

$$F_t = \frac{I_t}{I_m + I_t} \quad (2)$$

While a more detailed analysis is required to convert these relative phase fractions to volume fractions [6], this simplified approach is adequate for most studies

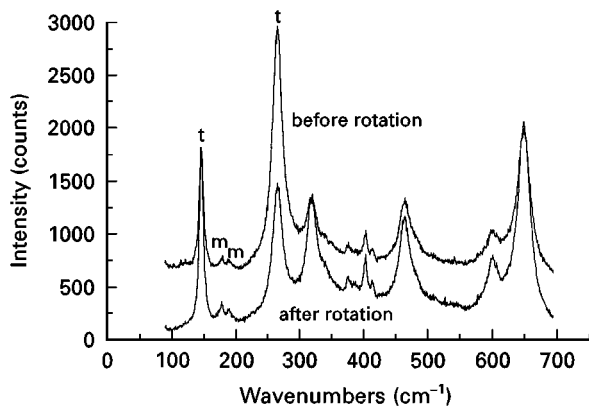


Figure 1 Spectra obtained by (a) before rotation, and (b) by rotating the grain through 90°: (m) monoclinic, (t) tetragonal.

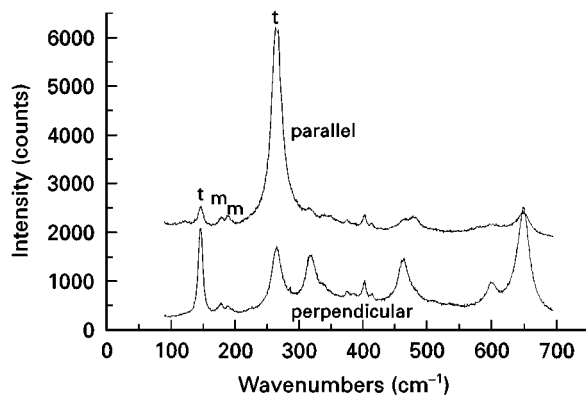


Figure 2 Spectra obtained from a single grain (a) parallel to, one (b) perpendicular to the laser polarization direction: (m) monoclinic, (t) tetragonal.

in which the change in phase content of PSZ ceramics is monitored in relation to changes in other physical properties.

3. Results and discussion

Spectra obtained using single laser polarization and rotating the grain through 90° between the spectra being collected were very different (Fig. 1). Spectra obtained by changing the polarization of the laser but not rotating the grain were also very different (Fig. 2).

The changes in the spectra as the relative orientation between the laser polarization and the grain were altered are clearly illustrated by comparing the intensity of the tetragonal peak at 265 cm⁻¹ to the intensities of the other peaks. In Figs 1 and 2 the intensity of the peak at 265 cm⁻¹ relative to those of the other peaks is greatest before the grain is rotated and when the laser polarization and the analyser are parallel. When the laser polarization and analyser are in the perpendicular configuration the relative intensity of the peak at 265 cm⁻¹ decreases.

Another notable change in the spectra obtained is shown in Fig. 2. It can be seen that, as the polarization of the laser changes from parallel to perpendicular, the relative intensities of the peaks comprising the monoclinic doublet at 180 and 190 cm⁻¹ also change. In the parallel arrangement, the peak at 190 cm⁻¹ is

TABLE I Quantitative analyses for a single grain, orientation of laser polarization and grain varied

Description	F_m	F_t
Parallel	0.019	0.981
Perpendicular	0.063	0.937
Rotated 90°, parallel	0.008	0.992
Rotated 90°, perpendicular	0.050	0.950

TABLE II Comparison of quantitative analyses for four different grains of MS grade Mg-PSZ

Grain	F_m	F_t	Standard deviation
1	0.035	0.965	0.026
2	0.041	0.959	0.019
3	0.038	0.961	0.018
4	0.038	0.962	0.027
All spectra	0.038	0.962	0.021

more intense while in the perpendicular arrangement the peak at 180 cm⁻¹ is the more intense.

The results for quantitative analyses of spectra obtained from a single grain are shown in Table I. Two spectra, one with the laser polarization and the analyser parallel, and one with them perpendicular were collected (denoted “parallel” and “perpendicular”). These are the spectra shown in Fig. 1. The sample was then rotated through 90° and the process repeated (“rotated 90°, parallel” and “rotated 90°, perpendicular”, Fig. 2). Three other grains were characterized in the same way. As can be seen from Table I, the quantitative results of spectra collected from a single grain can be significantly different.

The results of all quantitative analyses of the spectra are shown in Table II. If the four spectra (“parallel”, “perpendicular”, “rotated 90°, parallel” and “rotated 90°, perpendicular”) are collected and the quantitative results averaged, as in Table II, then the average results from grain to grain become more consistent even though the individual results from a single grain can be quite different.

The dependence of the micro-Raman spectra on the orientation of the grain being analysed relative to the polarization of the laser, is due to the small volume of material from which the spectra are collected. Ishigame and Sakurai [8] found that the Raman spectrum obtained from a single monoclinic crystal of ZrO₂ depended on the orientation of the crystal. (No changes were made to the polarization of the laser).

In each grain of Mg-PSZ the tetragonal precipitates have three variants and the monoclinic particles have 24 variants [9]. It is not surprising therefore that the use of a small sampling volume results in orientation dependent spectra because light is scattered from only three tetragonal variants and 24 monoclinic variants. The small number of sampled tetragonal variants compared to monoclinic variants is the reason why the dependence of the spectrum on the orientation of the grain relative to the polarization of the laser is more marked in the tetragonal peaks than it is for the monoclinic peaks.

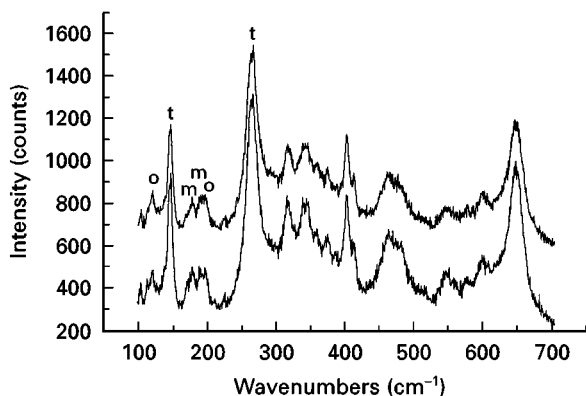


Figure 3 Two macro-Raman spectra from the same wear track on MS grade Mg-PSZ: (m) monoclinic, (o) orthorhombic, (t) tetragonal.

Authors performing quantitative analysis of Mg-PSZ have not remarked on the orientation dependence of the spectra collected from other micro-Raman spectrometers for two reasons. The first of these reasons is that there is expected to be a difference in the amount of transformation from grain to grain following mechanical testing. This arises from differences in the directions of the tetragonal precipitates with respect to the critical resolved shear stress and variations in the stress levels within grains due to stress gradients within the sample. It is not surprising therefore, to find some differences in the spectra obtained from different grains. The second reason is that there is no standard micro-Raman spectrometer and incident beam widths can range from 1 to 2 μm [5] to 20 μm [2]. Beam widths of 20 μm would lead to scattered light being collected from more than one grain and hence such a spectrometer configuration would be more likely to produce a spectrum averaged over many more precipitate orientations.

The very small collection volume used in the present micro-Raman experiments made the orientation dependence of the spectra very obvious. It was found that reasonably consistent spectra could be obtained by using a 10 \times objective lens. In this case the sampling volume is estimated to be 20 μm wide and 40 μm deep, large enough to include scattered light from more than one grain. The consistency of the spectra improved as the beam width was increased. Macro-Raman spectra obtained using a beam width of 1 mm on a MS Mg-PSZ sample that had been subjected to wear testing [10] were very nearly identical regardless of

the orientation of the sample or where on the wear track the beam was placed (Fig. 3).

4. Conclusions

The crystallographic orientation of the grain being sampled relative to the polarization of the laser greatly affects the Raman spectrum obtained. The effect is greatest when the sampled volume of material is small. Reasonably reproducible Raman spectra can be obtained by averaging spectra obtained by rotating the sample and/or the laser polarization or by using a sampling volume approximately 20 μm wide and 40 μm deep in Mg-PSZ with a grain diameter of 25–30 μm .

Acknowledgements

The support of the Australian Research Council (ARC) and the Department of Employment, Education, Training and Youth Affairs (DEETYA) through the provision of an APA(I) scholarship for GLK, in conjunction with ICI Australia Operations Pty. Ltd is gratefully acknowledged. The Raman experiments were performed with the assistance of Dr Kerry Nugent on the spectrometer in the School of Physics, University of Melbourne, Parkville, funding for which was provided by an ARC (Mechanism C) grant.

References

1. D. R. CLARKE and F. ADAR, *J. Amer. Ceram. Soc.* **65** (1982) 284.
2. D. B. MARSHALL, M. R. JAMES and J. R. PORTER, *ibid.* **72** (1989) 218.
3. M. BOWDEN, G. D. DICKSON, D. J. GARDINER and D. J. WOOD, *J. Mater. Sci.* **28** (1993) 1031.
4. R. H. DAUSKARDT, D. K. VEIRS and R. O. RITCHIE, *J. Amer. Ceram. Soc.* **72** (1989) 1124.
5. D. B. MARSHALL, M. C. SHAW, R. H. DAUSKARDT, R. O. RITCHIE, M. J. READEY and A. H. HEUER, *ibid.* **73** (1990) 2659.
6. C. S. LIM, T. R. FINLAYSON, F. NINIO and J. R. GRIFFITHS, *ibid.* **75** (1992) 1570.
7. T. R. FINLAYSON, A. K. GROSS, J. R. GRIFFITHS and E. H. KISI, *ibid.* **77** (1994) 617.
8. M. ISHIGAME and T. SAKURAI, *ibid.* **60** (1977) 367.
9. B. C. MUDDLE and R. H. J. HANNINK, *ibid.* **69** (1986) 547.
10. G. L. KELLY and T. R. FINLAYSON, in preparation.

Received 6 October 1997
and accepted 11 May 1998