

X-ray Line Broadening Study on Shock-modified Zirconia*

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Abstract

Zirconia (ZrO₂) powder compacts have been subjected to controlled, quantitative high pressure shock loading at peak pressures from 5–27 GPa and preserved for post-shock analysis. The overlapping broadened X-ray diffraction peak profiles have been separated by least-squares fitting procedures. The separate lines have been analysed in the usual manner to determine the residual lattice strain and the coherent crystallite sizes. Maximum modification effects are observed near 20 GPa with strain values near 3×10^{-3} and size values near 200 Å.

1. Introduction

The use of high pressure shock compression to modify the microstructure, achieving unique properties and enhancing solid state reactivity in various materials, has recently been of great interest and has led to chemical synthesis of some compounds (Graham *et al.* 1986, and references therein). Materials subjected to such high pressure loading have been shown to contain a high level of defects with large retained lattice strains, even for highly refractory materials (Morosin 1987). X-ray diffraction profile analysis provides a means of determining the residual lattice strain and the coherent crystallite size resulting from such defects. These studies on shock-modified zirconia are part of a larger study on shock-induced solid state chemistry involving pure ZrO₂ powders as well as mixtures with PbO (Hankey *et al.* 1982; Morosin *et al.* 1984; Hammetter *et al.* 1984).

The basic principles for the analysis of X-ray diffraction peak profiles are well known and have been examined and discussed elsewhere (Delhez *et al.* 1982, and references therein). The application of such analysis to a large number of materials has raised several materials issues, such as effects of crystalline anisotropy (Morosin and Graham 1984, 1985), as well as procedural issues. Examples of procedural issues include the proper method to evaluate (1) overlapping lines resulting from the symmetry of the material, (2) new phases generated by the shock event, and (3) closely spaced lines which upon broadening overlap. In the present case, zirconia partially converts to the tetragonal phase under shock compression (Morosin *et al.* 1984). This led to our development of new computer programs as well as computer modelling to define better parameters and procedures to use in profile analysis (Zhang *et al.*

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1988). Analysis of the broadened profiles on shock-modified zirconia are reported in the present paper.

2. Experimental

The zirconia powder used was a commercially available material (Teledyne Wah Chang, Lot SP 97310 Å). This material exhibited a reasonably sharp X-ray diffraction pattern, typical of a material with at least a 2000 Å crystallite size. This material was assumed to have negligible residual strain and served as our standard in order to determine the instrumental broadening for our peaks.

The samples were subjected to controlled shock compression with the 'Bear' explosive-loading fixtures (Graham and Webb 1984). The zirconia powder was pressed in place into compacts with densities between 50% and 60% of theoretical solid density within copper capsules of the sample recovery system. The fixtures were then subjected to either explosive or gas-gun driven projectile-loading. Both techniques lead to controlled, quantifiable, shock-wave loading conditions. The capsules were designed to form an air-tight seal. After retrieval of the gas-tight sealed capsules from the recovery fixtures, they were sawed and pressed open. The recovered powder was separated into samples taken from locations within the capsule. Such samples were lightly ground to break up agglomerates if present before further characterisation.

Table 1. Schedule of shock compression experiments

Experiment	Fixture	Impactor	Density ^A (Mg m ⁻³)	Peak pressure ^B (GPa)	Mean bulk temp. ^B (°C)
1868	Gun	256 m s ⁻¹	3.45	~5	~40
1898	Gun	396 m s ⁻¹	3.12	12	200
38G826	Momma Bear A	Baratol	3.17	16	300
8G820	Baby Bear	Comp B	3.26	20	250
36G826	Momma Bear A	Comp B	3.14	22	425
18G820	Baby Bear	Comp B	3.26	27	525

^A Initial sample powder compact density.

^B See Section 2 and Graham and Webb (1984, 1986).

Quantification of pressure and temperature conditions within the compacts has been achieved with an extensive program of numerical simulation using a two-dimensional computer code that describes the pressure-temperature history as the shock-wave propagates in the sample (Graham and Webb 1984, 1986). Various pressure and temperature pulses were obtained by varying the fixture size, projectile velocity and load or explosive configuration, and initial packing density of the zirconia powder. These conditions are detailed in the schedule of shock-modification experiments as shown in Table 1. The peak shock pressure varies from a value of 5 to 27 GPa.

X-ray diffraction was used to characterise the zirconia powders. Initial surveys (nickel filtered Cu K α radiation and a standard 114.5 mm Norelco powder camera) showed the relative broadening of the diffraction lines for the various samples. In addition, conversion to and recovery of the tetragonal form of zirconia was noted in the post-shock samples.

The peak profiles of the X-ray diffraction lines for the zirconia were obtained with a Siemens D-500 automated diffractometer equipped with a monochromator on the detector set so that both α_1 and α_2 lines were collected. The aperture and

diffraction slits were 1° and those adjacent to the diffracted beam monochromator were both 0.15° . The intensity data were taken by stepping increments of 2θ equal to 0.010° with fixed time counting depending on the intensity of peak. Our counting statistics reflected requirements set upon the instrument for other uses and represents a compromise of several factors including our fitting procedure described below. The various (hkl) peaks measured are indicated below (see top of Figs 2 and 3 in Section 4). Since the lines for this monoclinic material are rather close together, severe overlapping occurs upon broadening due to shock modification. This problem necessitated the development of a more stringent protocol for data collection. However, the original data were used for this study.

3. Profile Analysis

Our two new computer codes developed for analysis of broadened profiles are a profile fitting program, XRAYL, and a profile deconvolution and analysis program, CRY Siz. XRAYL allows the fitting of observed profiles which may consist of one or more diffraction lines by one of four mathematical functions, Gauss, Cauchy, Voigt or Pearson VII. XRAYL produces smooth reference and broadened profiles for use by CRY Siz, and is also particularly useful for separating close lines which may overlap as in our shock-modified zirconia. Another important feature is that the program provides the ability to force every unique line to cover the same span of $1/d$ space. This variable a_3 , described by Warren (1969), is selected with a particular value and produces comparable background regions in $1/d$ space for all lines. Hence, a_3 is equal to $\lambda/4(\sin\theta_1 - \sin\theta_0)$, where θ_1 and θ_0 are the position of the high angle limit and the peak maxima respectively. We refer to this span as a 'window'. This program is ideal for carrying out computer modelling to ascertain the importance of various experimental and computational procedures employed on the raw profiles of the diffraction lines. Such modelling has shown the importance of obtaining fitted profiles which achieve a nominal 'background' value on both sides; otherwise, serious errors will result in the subsequent calculations of size and strain values (Zhang *et al.* 1988).

CRY Siz carries out the steps necessary on the profiles from XRAYL to obtain the size and strain information. Such peaks may be those obtained by the mathematical functions (see above) or the natural data points augmented only with respect to the points describing the background in order to achieve the desired window. CRY Siz deconvolutes the instrumental broadening by the usual Stokes (1948) Fourier transform method. The Fourier coefficients (free from instrumental broadening) are used for the subsequent steps to calculate the size and strain information using the Warren-Averbach model. They are also used to obtain complimentary values as determined by older traditional Hall-Williamson or Gauss-squared methods (Warren 1969; Delhez *et al.* 1982; Morosin and Graham 1984; Morosin 1987) by plotting B versus s or B^2 versus s^2 respectively, where $B = \beta \cos \theta / \lambda$ and $s = \sin \theta / \lambda$, and β is the line breadth (discussed below). For these latter methods, we have employed the back Fourier transformed line, using the coefficients corrected for instrumental broadening, so as to have a line profile on which values of β (either determined as the full width at half maximum, the integral breadth or the second moment) can be determined. Such values determined on the corrected line profiles can then be used for the traditional plotting methods. In addition, the usual multiple-line Warren-Averbach procedure examines a particular X-ray line and its second order, for example the (012) and (024) as a pair. In this study, such pairs were not observed due to the complexity of the powder

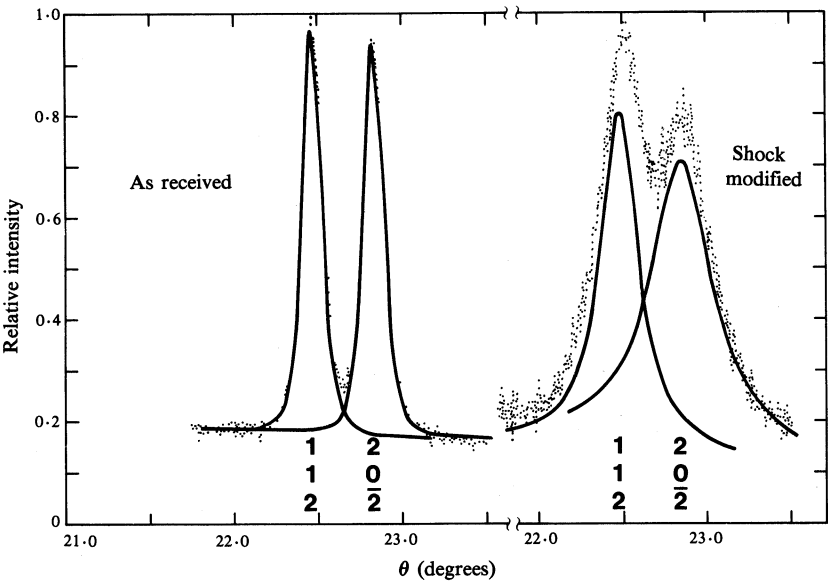


Fig. 1. Plot of the (112) and (202) X-ray lines for zirconia for our standard (instrumental broadened) and shock-modified (27 GPa) samples. The solid curves shown are the Pearson VII function line profiles for the two individual peaks, the sum of which is a least-squares fit to the data points.

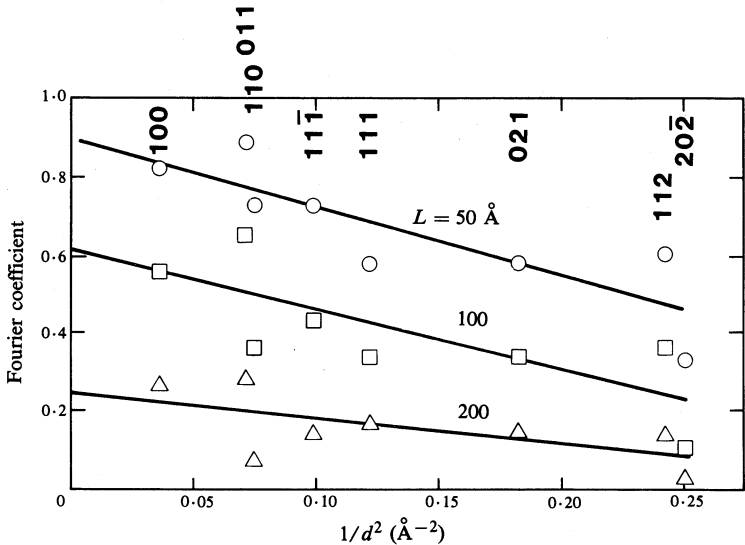


Fig. 2. Warren-Averbach (WA) Fourier coefficients as a function of interplanar spacing for the shock-modified sample 8G820 (20 GPa). A least-squares line through the data points is shown for each of the three L values.

pattern; however, the entire set of lines was considered as a single group. This is accomplished by employing $1/d^2$ rather than the conventional order of the index (Warren 1969; Morosin 1987). This results in average strain and size values compared with those obtained along specific directions for the usual profile fitting analysis. In addition, the small peak corresponding to the tetragonal phase material formed at higher shock pressures has been removed. This peak grows in size above 15 GPa, as a broad peak corresponding to a crystallite size of approximately 90 Å.

4. Results

Fig. 1 shows a comparison of two peak profiles, the (112) and (202̄), of zirconia for the as-received and shock-modified (27 GPa) samples. The solid curves are the Pearson VII function fit used in this example. Our subsequent computer modelling suggests a wider 'window', a_3 , is necessary for the fitting of the broadened lines. Such Pearson VII function fits were used for all results reported here.

Fig. 2 shows a typical plot of the Warren-Averbach (WA) Fourier coefficients as a function of the square of the reciprocal of the interplanar spacing d . Such Fourier coefficients were obtained using CRYSTIZ and have had the instrumental broadening contribution removed. This is for the 20 GPa shock-loaded sample (8G820). Data are shown for three values of L , where L is the distance along the perpendicular to the reflecting lattice planes (hkl) whose spacing is d . The straight lines for each particular L value correspond to a least-squares line and the intercept would result in an 'average' size Fourier coefficient, while the slope would yield an 'average' mean-square strain value. For other shock-modified materials, a pattern (or systematic deviation of the points from the straight line) for various (hkl) values is observed as one compares different shock-loaded samples with each other. This is believed to result from elastic anisotropy (Morosin 1987). However, in our zirconia samples, such patterns

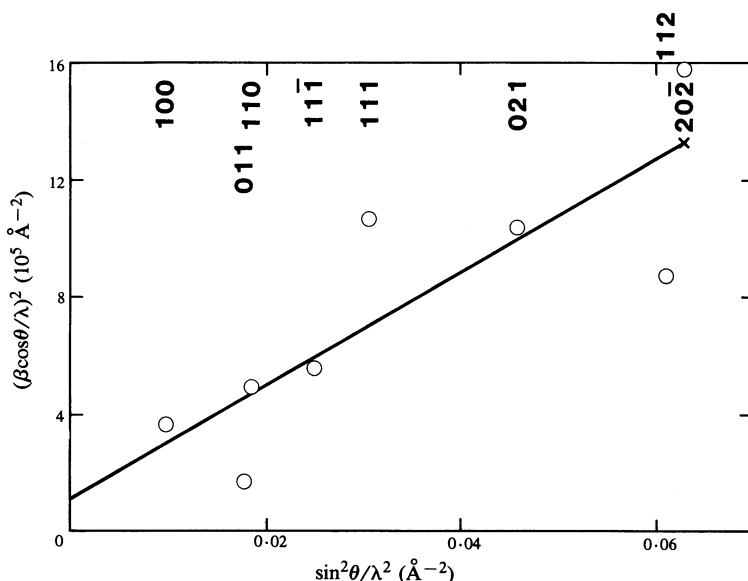


Fig. 3. Gauss-squared plot, for size and strain separation, with β values obtained from the second moment on back-transformed profiles for sample 8G820.

are not as consistent from sample to sample. This probably results from contributions to the line profile resulting from the method used to separate the overlapping peaks.

Another way in which elastic anisotropy can be seen is through the use of the traditional plotted procedures mentioned above. The departure from the straight line behaviour results from a combination of such anisotropy contributions and of errors in the data processing (experimental as well as evaluation of the line breadth parameters). Fig. 3 shows the second moment data obtained on back

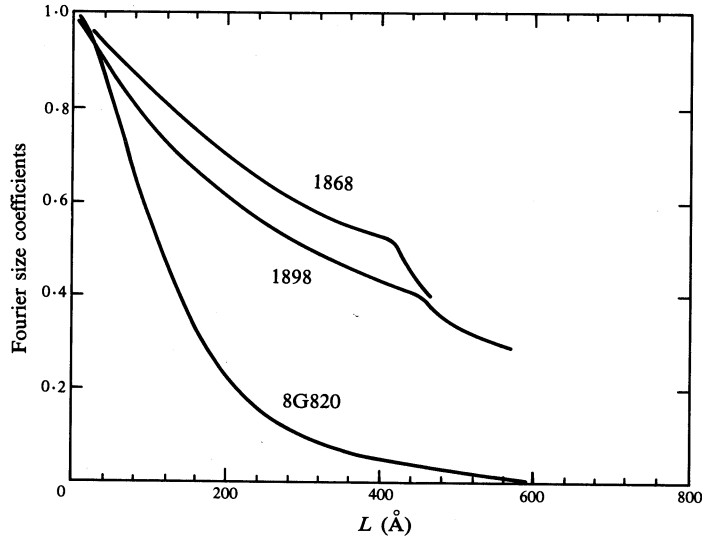


Fig. 4. Comparison of the WA size coefficient versus length L for three shock-modified samples. Smooth curves have been drawn through our points.

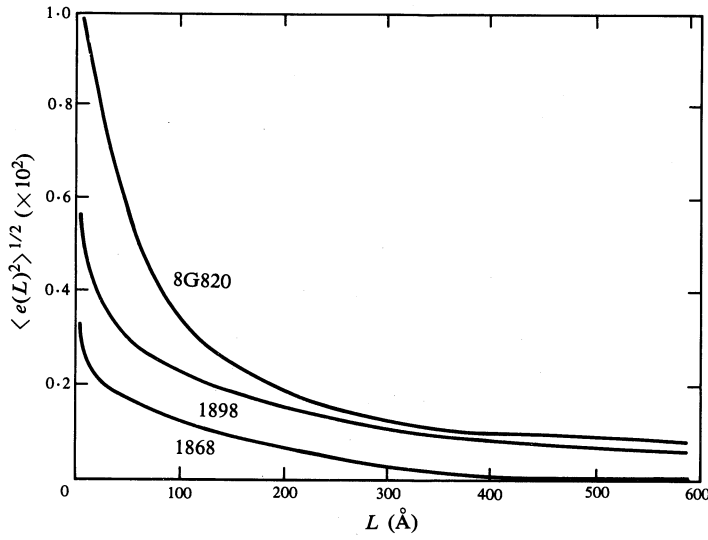


Fig. 5. WA strain values versus length L for three shock-modified samples. Smooth curves have been drawn through our points.

Fourier transformed lines, so that the instrumental broadening has been removed, on the 20 GPa shock-modified sample (8G820). Since our previous modelling on synthetically broadened, overlapping lines shows good linear behaviour on such plots, we believe the departure from the least-squares line is primarily due to elastic anisotropy, which unfortunately we currently cannot evaluate without having data on higher order reflections. Thus, average values are obtained. Here, the least-squares line shown yields an intercept and slope corresponding to a crystallite size D_G and strain e_G . These values are $D_G = 329 \text{ \AA}$ and $e_G = 1.1 \times 10^{-2}$. Such values are usually different from those obtained by the WA procedure, as has been discussed by various authors (Delhez *et al.* 1982; Morosin 1987).

Figs 4 and 5 show the WA size coefficient and strain values respectively, obtained for three samples (8G820, 1868 and 1898). The size coefficients shown in Fig. 4 are obtained from the intercepts for particular L values as illustrated in Fig. 2. Values shown in Fig. 4 correspond to samples selected to exhibit a wide range of shock-pressure effects. With increasing shock pressure, the curves fall off faster corresponding to shorter coherent crystallite sizes. The curves not shown essentially follow a similar behaviour. As these curves show, there is a slight hook effect evident. Such hook effects have been shown from our computer modelling to arise from several anomalies on the raw data, one of which is particularly important and that is the proper evaluation of the background. Since the background values were extended to proper 'window' $a3$ values taking into account the proximity of the neighbouring peaks, the contribution an improperly evaluated background makes to the hook effect has essentially been eliminated even for our severely overlapped peaks. Values for the WA or average-area-weighted size $\langle Da \rangle$ may be obtained from extrapolation at small L values of the curves shown and are given below in Fig. 6.

In Fig. 5, the WA strain values are shown for the same samples as in Fig. 4. With increasing shock pressure, these curves are higher over the entire range of L values. The general shape of such strain curves are typical of those for cold worked metals, of milled ceramics and of shock-modified materials. Such curves show that strains, averaged over short distances, are great and decrease or die out as they are averaged over larger coherent diffracting domains (Delhez *et al.* 1982).

Figs 6 and 7 summarise the WA size and strain values as a function of shock pressure. The strain values e_L are obtained by averaging the values of $\langle e^2(L) \rangle$ (Fig. 5) for L from 10 \AA to the appropriate average-area-weighted size $\langle Da \rangle$ (shown in Fig. 6). This shock-pressure behaviour is similar to that observed in alumina (Morosin and Graham 1984) in that the size decreases and the strain increases with pressure; however, the values tend to saturate (and possibly turn over with respect to strain) at higher shock pressures. Other materials, such as AlN also tend to saturate at higher shock pressures (Morosin 1987).

If the strain actually decreases with increasing pressure, it exhibits a behaviour similar to that observed in several other shock-modified materials. In rutile, titanium carbide and hematite, the experimental data suggest that a shock-temperature effect occurs which causes the primary shock-pressure changes to be reversed (annealed) (Morosin 1987; Zhang *et al.* 1987). The shock temperature may be controlled by varying the initial packing density of the sample, and as this temperature increases along with shock pressure two effects on residual strain of recovered materials are observed. First, in some hard refractories, more plastic deformation can occur under shock-loading at the same mean peak shock pressure when there results a higher

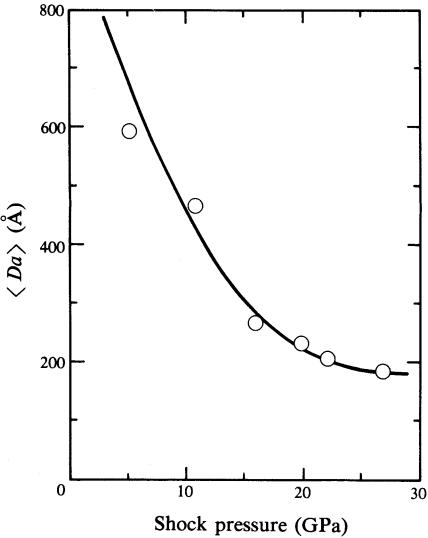


Fig. 6. Values for the WA size for all our shock-modified samples shown as a function of shock pressure.

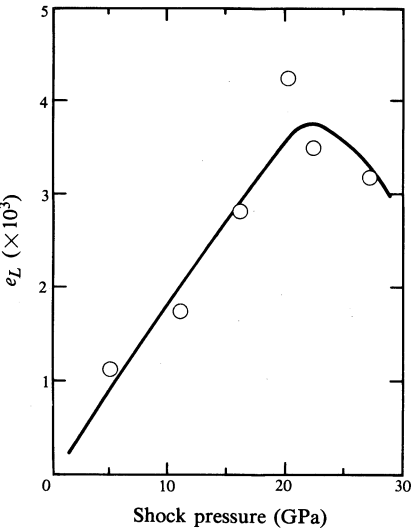


Fig. 7. Values for the WA averaged strain versus shock pressure.

shock temperature. Second, the effect of shock temperature may be sufficient for particular materials to result in an annealing effect. The annealing effect is sufficient to reduce strain, increase crystallite size and reduce defect level concentrations as measured by other means, e.g. electron paramagnetic resonance or specific heat.

5. Concluding Remarks

Shock-modified zirconia shows large changes in crystallite size and residual strain which are a function of shock-compression parameters. These defects are accompanied by the conversion of some of the material to the tetragonal phase (Morosin *et al.* 1984). These defects also constitute a significant amount of energy, trapped in the

lattice, which upon heating influences the monoclinic to tetragonal transformation temperature (Hammetter *et al.* 1984). In addition, such shock-modified zirconia exhibits enhanced reactivity, reducing the PbO-ZrO_2 reaction temperature (Hankey *et al.* 1982). The shock modification results presented here should prove valuable in assessing the effects of shock-induced chemistry in more complex systems, as well as providing part of the basis for modelling chemical reactions under shock compression (Horie and Kipp 1987).

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