Experimental shock deformation in zircon: a transmission electron microscopic study

H. Leroux a, W.U. Reimold b,*, C. Köberl c, U. Hornemann d, J.-C. Doukhan a

a Laboratoire de Structure et Propriétés de l’Etat Solide, Université des Sciences et des Technologies de Lille, 59655 Villeneuve d’Ascq, France
b Economic Geology Research Unit, Department of Geology, University of the Witwatersrand, Private Bag 3, P.O. Wits 2050, Johannesburg, South Africa
c Institute of Geochemistry, University of Vienna, Althanstr. 14, A-1090 Vienna, Austria
d Fraunhofer Institut für Kurzzeitdynamik, Hauptstr. 18, D-79576 Weil am Rhein, Germany

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Abstract

In recent years, apparently shock-induced and, thus, impact-characteristic microdeformations, in the form of planar microdeformation features and so-called strawberry (granular) texture, have been observed in zircons in rocks from confirmed impact structures and from the K/T boundary. The nature of the planar microdeformations in this mineral is, however, still unknown, and critical information is needed regarding the shock pressure range in which these deformation effects are produced. We experimentally shock deformed two series of thin zircon (ZrSiO₄) target plates, cut perpendicular to the c-axis, at shock pressures of 20, 40, and 60 GPa. The recovered samples were characterized by optical and scanning electron microscopy. In addition, one sample series was studied by transmission electron microscopy (TEM). Microdeformation effects observed at 20 GPa include pervasive micro-cleavage and dislocation patterns. Plastic deformation is indicated by a high density of straight dislocations in glide configuration. The dominant glide systems are <100>{010}. Micro-cleavages, induced by shear stresses during the compression stage, occur mostly in the {100} planes. The large density of dislocations at crack tips shows that plastic deformation was initiated by the micro-cracking process.

At 40 GPa, the sample was partly transformed from the zircon (z) to a scheelite (CaWO₄)-type (s) structure. Planar deformation features (PDFs) containing an amorphous phase of zircon composition are present in the not yet transformed zircon relics. The phase with scheelite structure, initiated in the {100} planes of zircon, consists of thin (0.1 to several μm) bands that crosscut the zircon matrix. The phase transformation is displacive (martensitic) and can be related by {100}, // [112], and [001], // <110>. The scheelite structure phase is densely twinned, with twins in the (112) plane. The 60-GPa sample consists completely of the scheelite structure phase. Crosscutting and displacing relationships between twins and PDFs demonstrate that PDFs are formed in the zircon structure, i.e., before the phase transformation to the scheelite structure occurred, most likely at the shock front. Crystallographic orientations of optically visible planar features in zircon, in comparison with orientations of planar defects at the TEM scale, suggest that the optically visible features are more likely planar microfractures than PDFs. © 1999 Elsevier Science B.V. All rights reserved.

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* Corresponding author. Fax: +27-11-339-1697; E-mail: 065wur@cosmos.wits.ac.za

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1. Introduction

Deformation effects have been identified in zircon crystals from impact breccias or shock metamorphosed basement rocks at a number of confirmed impact structures and several K/T boundary sites (e.g., [1–5]). In some impact structures — especially large and old/eroded ones such as the Vredefort Structure — planar deformation features (PDFs; e.g., [6,16–18]), the most widely known and most important shock metamorphic indicator phenomenon in quartz and other rock-forming minerals, have been adversely affected by post-impact thermal and hydrothermal processes (e.g., [6]). In such cases, shock effects in zircon, a mineral which is much more refractory and resistant to alteration than most other minerals, such as quartz or feldspars, may have great potential as a tool for the determination and characterization of impact deformation.

Apparent shock effects in zircon, such as the occurrence of ‘planar features’ and of so-called ‘strawberry or granular texture,’ which is composed of numerous submicroscopic, idiomorphic zircon crystallites of generally common growth orientation and most likely grown at the expense of a melted parent crystal, are now widely known and accepted as shock (impact) characteristic effects. However, the true nature of these planar features is not yet understood (e.g., [5,7]). It is not clear if they represent an equivalent of planar deformation features (PDFs), as known from other rock-forming minerals, or are planar fractures, or some other deformation effect. In contrast to this problem, it is well-known that zircon undergoes a phase transformation to a phase with scheelite structure under static compression [8,9] and under shock compression at pressures in excess of 30 GPa [7,10–12]. The high-pressure polymorph survives to relatively high temperature, up to 1000°C [11], and should be a good indicator for impact deformation in terrestrial crustal rocks.

Another reason why the mineral zircon is of special interest in the context of impact cratering studies is the general acceptance of the importance of this mineral for the accurate (in terms of geological time) dating of geological events, including impact events [2–5,13–15]. Consequently, zircon separated from impact melt rocks might provide unshocked authigenic zircon crystals that could be utilized to date the formation of the melt rock and, by implication, the impact event. Zircon separates of shocked/potentially shocked country rocks may reveal critical information regarding the presence of an impact structure or information regarding the degree of shock deformation of such material.

In order to address the nature of crystal lattice defects in shocked zircon and to investigate the shock pressure ranges in which different types of shock deformation would form in zircon, we performed a series of shock experiments at pressures of 20, 40, and 60 GPa.

2. Experimental procedure

Two natural zircon crystals, of about 1 cm length and about 0.5 and 0.7 cm width, respectively, from Sri Lanka and Australia (Fig. 1) were cut perpendic-
ular to the $c$-axis in order to have the shock propagation direction parallel to the $c$-axis in all shock experiments. Shock recovery experiments were performed on zircon sections of about 1 mm thickness, which were embedded in potassium iodide, using the shock reverberation technique at the Fraunhofer Institute (e.g., [7,12]). The samples were shocked to pressures of 20, 40, and 60 (nominally 59) GPa. Thin sections of the shocked samples were studied optically and by scanning electron microscopy. One sample set was also analyzed by transmission electron microscopy (TEM). Specimens for TEM analysis were prepared by ion bombardment until electron transparency was reached. TEM examination was carried out with a Philips CM30 (300 kV) instrument, equipped with an energy-dispersive X-ray spectrometer (EDS), at the Université de Lille.

3. Results

3.1. Optical and SEM observations

At the scale of the optical microscope, the deformation of the unshocked zircon is revealed as normal, widely-spaced (>tens of $\mu$m) cleavage and limited, irregular fracturing. At 20 GPa, irregular fracturing and, especially, cleavage are strongly enhanced, but grain rotation has not occurred. At 40 GPa, the fracture pattern is even denser, and so-called 'shock fracturing' — known from quartz shocked at pressures of <8 GPa (e.g., [16]) — is locally developed. At high magnification, sets of planar features with spacings of one to a few $\mu$m, are abundant between the wider-spaced cleavages. At 60 GPa, the density of planar features is further enhanced. In these samples we also find irregular fractures that are more abundant than in the other samples, and the crystal structure has been ubiquitously distorted, resulting in mosaicism at the tens of $\mu$m scale. At the SEM scale, several sets of planar features at 45° to each other (probably corresponding to planes of the {112} zone) were detected in the 40-GPa and 60-GPa samples. They are spaced at 10–50 $\mu$m, are about 1–1.5 $\mu$m wide, and do not appear as open fractures.

3.2. Transmission electron microscopy

3.2.1. 20-GPa sample

Microdeformation in the 20-GPa sample examined by TEM mainly consists of pervasive dislocations and numerous micro-cracks. Brittle deformation is indicated by numerous straight and parallel fractures (Fig. 2a), oriented particularly parallel to (100), (010), and (111), but also sometimes parallel to (110) and (310). These fractures are <$50$ nm wide and are interpreted as micro-cleavage planes. Typically, these fractures are terminated by dislocations, indicative of stress concentration at fracture tips. This implies that plastic deformation was initiated by the micro-cracking process.

Plastic deformation is evident from an abundance of straight dislocations in glide configuration (Fig. 2b). The dislocation density is on the order of $10^{14}$ m$^{-2}$ and is relatively homogeneously distributed, although it reaches higher values in some areas ($>10^{15}$ m$^{-2}$). Two major glide systems were activated, for which the Burgers vectors were identified using standard diffraction±contrast analysis.

These dislocations have the Burgers vectors [100] and [010] (which are equivalent with respect to the tetragonal structure of zircon). The line orientations for these dislocation systems are [100] and [010], respectively, showing that these dislocations are of the screw type. Dislocation densities may be enhanced in narrow, straight 'micro-bands,' the orientations of which indicate that the glide systems activated are [100](010) and [010](100) (Fig. 2c). These glide systems are equivalent in the zircon structure and, thus, can be denoted as $<100>{010}$.

The orientations of glide planes and micro-cracks are probably related. The dislocation density increases near cracks (e.g., Fig. 2d), suggesting that cracks play the role of nucleation sites for the generation of dislocations at fracture tips (cracks are areas of stress concentration). For the {111} microfracture plane, the Burgers vector of dislocations at crack tips is $<110>$, suggesting the presence of the glide system $<110>{111}$. Splitting into partials was observed for these dislocations, but further comprehensive characterization of these dislocations was not carried out. Some observations suggest that dislocation interaction occurred during dislocation propagation (Fig. 2e).
Fig. 2. (a) A general view of the shock-induced defects in the 20-GPa specimen. Micro-cleavage is found mainly in the (100) planes; in addition, numerous straight dislocations in glide configuration are observed. (b) Dislocations in glide configuration, demonstrating that intense plastic deformation occurred during the shock deformation. The glide systems $\langle 100 \rangle \{ 010 \}$ are dominant. The long, straight dislocations are along the [100] and [010] directions and correspond to the two equivalent glide systems $\langle 100 \rangle (010)$ and $\langle 010 \rangle (100)$. (c) Dislocation densities are frequently enhanced in narrow, straight ‘micro-bands’, which correspond to the glide planes (100). (d) The dislocation density is significantly higher in the vicinity of cracks, showing that plastic deformation was initiated at crack tips. (e) Long and straight dislocations in glide configuration have the line orientation [100]. The short dislocations in ‘zig-zag’ form result from the interaction of dislocations belonging to the two dominant glide planes. The planar defects are micro-cleavage in (310) orientation.
3.2.2. 40-GPa sample

The studied sample is composed of a two-phase assemblage of materials having the zircon and scheelite structures. In zircon, the microstructure is similar to that of the 20-GPa sample, showing the same micro-cleavage and dislocation arrays. There is no evident increase of dislocation density in the 40-GPa sample, although the peak pressure has increased by a factor of 2.

In addition to micro-cleavage and dislocations, very thin (<10 nm) planar defects were detected, which are composed of an amorphous phase (Fig. 3a). They correspond to the description of ‘planar deformation features’ in shocked silicates (e.g., [16–18]). These PDFs are present in low density (we detected only a few). Their crystallographic orientation is always close to the [320] planes.

A fraction of the zircon has been converted to a different crystal structure (Fig. 3b). The electron diffraction patterns obtained from this phase are consistent with the scheelite (CaWO_4) structure type, with a tetragonal unit cell with a = 4.7 Å and c = 10.5 Å (in contrast, the lattice parameters for the zircon structure are a = 6.6 Å and c = 5.98 Å). The zircon/scheelite volume fraction appears to be highly variable from area to area (though TEM is not the most suitable technique to record quantitatively the amount of transformed zircon due to poor

Fig. 3. (a) Planar deformation features (PDFs, arrows) in a plane roughly parallel to the (320) plane of zircon. To the right, a part of the sample converted to scheelite-structure phase. (b) A thick band of the scheelite-structure phase in crystallographic continuity with zircon. The scheelite phase is densely twinned in the (112) plane. (c) Thin scheelite-phase bands in {100} planes of zircon. The bands are parallel to the dislocation lines, illustrating the strong crystallographic control on the phase transition. (d) Electron diffraction pattern showing the epitaxial relationship between phases with scheelite and zircon structures (zone axis [001] for the zircon structure and [110] for the scheelite structure). Reflections formed according to the mirror twin law in the scheelite structure are present.
The scheelite phase occurs in the form of narrow (0.1 to several μm) bands within the zircon matrix. Where the bands of the scheelite phase are thin (typically 0.1 μm), they are parallel to the (100) plane of the zircon matrix (Fig. 3c). The larger bands commonly deviate from this orientation and penetrate the zircon matrix without obvious preferential orientation.

The scheelite-structure phase shows pervasive twinning, with twins typically 50 nm wide occurring in the (112) plane. There is a distinct crystallographic relationship between the zircon and scheelite-structure phases, which was examined by selected area electron diffraction. The relation between the orientations of the two structures was found to be as follows: the (100) plane of the zircon structure is parallel to the (112) plane of the scheelite structure, and the [001] direction of the zircon structure is parallel to the <110> direction of the scheelite structure (Fig. 3d).

3.2.3. 60-GPa sample

In the 60-GPa specimen, the zircon structure was completely converted to the scheelite structure. Fig. 4a shows a general view of this sample. No dislocations are detected, which indicates that plastic deformation is followed by the phase transformation. The scheelite-structure phase contains a very high density of twins of, on average, 50 nm width. These mechanical twins are oriented parallel to {112} planes, as indicated by the electron diffraction patterns (Fig. 4b).

In addition, 10–20 nm wide PDFs, characterized by amorphous lamellae fillings, are present (Fig. 4a and c). They are very straight and oriented along {110} planes of the scheelite structure. X-ray microanalysis showed that PDFs have the same chemical composition as zircon. A few observations of displacement of PDFs by twins were made, which suggest that PDF formation precedes that of twins (Fig. 4c).

Evidence for a previously reported [11] shock dissociation of zircon to ZrO₂ + SiO₂, which, according to these authors, should begin above 53 GPa, was not detected. Baddeleyite, presumably formed by impact-generated shock dissociation of zircon, is also known from tektites and impact glasses (e.g., [28]). In static pressure experiments [9], this phase transformation from the scheelite-structure phase to baddeleyite + SiO₂ was observed at pressures between ca. 20 and 50 GPa. In our 60-GPa sample, however, a polycrystalline aggregate of 20–100-nm sized crystals with scheelite structure was observed locally and might be an indication of incipient structural breakdown (Fig. 4d,e). One could also speculate that this texture could be an indication for new crystal growth (at the expense of a primary crystal) — which is the presumed mode of formation of the strawberry texture observed at the optical scale.

4. Discussion

4.1. Dislocations and micro-cleavage in the untransformed zircon

The dislocations observed in the 20- and 40-GPa samples are clearly related to shock-induced plastic deformation in zircon. The two dominant glide systems are <100>{010}. The Burgers vectors <100> represent the shortest translation vectors (6.6 Å) in the {100} planes, and one of the shortest in the zircon structure. The glide plane orientations are also easily reconcilable with the crystal structure of zircon, which consists of chains of edge-sharing, alternating SiO₂ tetrahedra and ZrO₈ dodecahedra parallel to the c-axis. Laterally, the chains are joined by edge-sharing ZrO₈ dodecahedra, parallel to the a- and b-axes [19]. The presence of chains of edge-sharing tetrahedra and dodecahedra parallel to the [001] direction accounts for the characteristic crystal habit in zircon, with faces that are mostly parallel to the c-axis ([110] and [100]). The chains are also responsible for the dominant [110] cleavage [19]. Accordingly, the fact that the dislocation glide planes follow {100} is not surprising, because the {100} planes are parallel to the [001] chains. Dislocation motion in these glide planes leaves the chains along the c-axis unaffected. In addition, the {100} planes are closely packed, and glide of dislocations on these planes does not break Si–O bonds of the SiO₄ tetrahedra.

In contrast to experimentally shocked diopside, in which severe multiplication of dislocations occurs as the result of the activation of Frank–Read sources [20], micro-cleavage (cracks) and dislocations in zir-
Fig. 4. (a) General view of the microstructure in the 60-GPa sample. The structure of zircon has been completely converted to the scheelite structure. Material with scheelite structure is characterized by a high density of twins and some PDFs (the one shown is in (110) orientation). (b) Electron diffraction pattern showing spots associated with the twins in (112). Zone axis = (170); t = twin. (c) PDFs oriented along (110) planes of the scheelite-structure phase. PDFs are displaced by twins, suggesting that PDF formation precedes twin formation. (d) Polycrystalline aggregate of 20–100-nm sized crystallites having the scheelite structure. (e) An electron diffraction pattern typical for such aggregates.
con are probably related. Indeed, a high density of dislocations is present at crack tips and suggests that crack tips are efficient nucleation sites for dislocations. Dislocations emitted from cracks propagate as sharply defined lines in the \( <100>\{010\} \) dominant glide systems. The nucleation of dislocations at crack tips facilitates the stress concentration near the crack tips and, furthermore, slows crack propagation. These observations attest to the important role played by brittle deformation in zircon. In shock deformation, fractures are known to be produced by the rarefaction wave of the shock process [17]. The rarefaction wave induces decompression and, thus, extensional fracturing. It is also possible that the micro-cleavage observed here is generated by shear stresses during the compression stage (resulting in shear fractures).

4.2. Phase transformation from the zircon to the scheelite structure

Transformation of zircon under high pressure into a phase with scheelite structure has already been observed in static deformation experiments [8,9], at ca. 12 GPa, and under shock compression [10,11,21]. According to Kusaba et al. [11], the phase transformation in experimentally shocked zircon begins above 30 GPa and is completed above 53 GPa. Fiske et al. [21] produced 1–2% scheelite-phase at 20 GPa, 10–15% at 30 GPa, and 100% conversion at 52 GPa. The scheelite structure was measured to be approximately 10% denser than the zircon structure (at ambient conditions; [8,11,22]). The scheelite phase is metastable at ambient pressure [11]. As the transformation is achieved during the short time interval of shock loading, it is believed that the phase transformation is displacive [11,22]. The mechanism of the transformation in terms of atomic movements has been analyzed by Kusaba et al. [22]. The transformation is not accompanied by a change of coordination of Si and Zr cations, but by rotation of the SiO\(_4\) tetrahedra, which allows a more efficient atom packing in the scheelite structure.

The displacive (martensitic) nature of the phase transformation is also suggested by the present TEM observations. The scheelite-structure phase(s) was found in a close epitaxial relationship with zircon \( (z) \), with \( \{100\}_z \parallel /\{112\}_s \), and \( [001]_z \parallel /\{110\}_s \). The first relation involves the two equivalent directions \( <110> \) of the zircon structure, which are converted to the directions \( [110] \) and \( [001] \) in the scheelite structure. The transition from zircon structure to scheelite structure requires only minor atomic displacement, consistent with a displacive mechanism. The phase transformation was probably enhanced due to uniaxial compression. The TEM observations also reveal that the phase transformation starts in specific planes — the \( \{100\} \) planes — of the zircon structure. This is in accord with a large number of observations on shock-compressed solids, in which the deformation is localized in thin planar regions. The tendency for planar feature formation is also illustrated by the PDFs formed at 40 GPa and dislocation bands observed in the 20-GPa sample.

4.3. Occurrence of planar deformation features (PDFs)

Formation of PDFs is a common response of silicates submitted to shock deformation. For example, PDFs are formed in quartz (e.g., [17] and references therein), in feldspars [23], and in diopside [20,24]. Their presence in a rock is regarded as a diagnostic indication of hypervelocity impact (e.g., [16,25]). PDFs correspond to shock-induced amorphization along crystallographically determined planes. Amorphous lamellae at the nanometer scale have also been produced in static high pressure experiments (e.g., [26]). However, they have never been described from naturally deformed minerals other than those deformed under the extreme high-strain-rate/pressure conditions that are uniquely associated with hypervelocity impact. For a detailed discussion of shock and static deformation features, especially planar microdeformations, refer to Grieve et al. [25].

A PDF formation mechanism based on crystal structure instability has been proposed by Goltrant et al. [27]: PDFs result from elastic instabilities of the shear modulus of the quartz structure at high pressure. Because PDFs consist of matter amorphized under pressure, it is believed that they represent nucleation sites for high pressure phases. Our TEM observations clearly show that this is not the case in zircon. There is no correlation between the occurrence of PDFs and the high-pressure phase. PDFs are formed in the zircon structure before the scheelite-
structure phase is formed. This is clearly illustrated by the displacement of PDFs by scheelite-phase twins in the 60-GPa sample. The crystallographic orientation of PDFs in the two structures also reflects this sequence. PDFs are observed close to the {320} planes in zircon (40-GPa sample) and in the {110} planes in the phase with scheelite structure. This demonstrates that the PDFs are formed in the zircon structure, at the shock front, before the transformation into the scheelite-structure phase takes place. The phase transformation probably propagates with the shock front, as suggested by Goltrant et al. [27]. In this regard, it is not surprising to find the orientation of PDFs in zircon parallel to the direction of shock-wave propagation, as commonly observed in quartz (e.g., [18]).

4.4. Absence of shock dissociation into ZrO$_2$ + SiO$_2$

No evidence for decomposition of the zircon or scheelite-structure phase to ZrO$_2$ + SiO$_2$, as reported by Kusaba et al. [11] in their samples shocked at 53 and 94 GPa, could be detected in our 60-GPa sample. However, the 53-GPa sample of Kusaba et al. [11] was a powdered specimen, in which shock temperature enhancement could have occurred locally, because of the high sample porosity. Furthermore, the observation that dissociation to ZrO$_2$ + SiO$_2$ did not occur in our single-crystal sample is not surprising. It confirms that the breakdown of zircon is governed by temperature, and not only by the pressure of shock loading. We did, however, observe in the 60-GPa specimen very fine-grained aggregates of crystals having the scheelite structure, which may indicate incipient breakdown and perhaps represent a preliminary step to the formation of ZrO$_2$ + SiO$_2$.

4.5. Nature of optically visible planar ‘features’

One of the main aims of this investigation was to clarify the nature of optically identifiable planar defects in shock-metamorphosed zircon. It is not readily possible to compare directly optically visible planar microdeformations and defects observed at sub-micrometer dimensions at the TEM scale. However, one can compare the crystallographic orientations of features at these two different scales. Our initial observations of orientations of planar defects at the optical microscopic scale suggest that they are mainly formed parallel to the (201), (211), (221), (111), (100), and {hk0} planes. At the TEM scale, micro-cleavage parallel to several of these orientations has been described. In addition, the (100) and (010) planes may contain bands converted to scheelite-structure material. In contrast, PDFs observed at the nm scale were always parallel to {320} planes.

Thus, we interpret the optically resolved planar microdeformations as manifestations of shock-induced cleavage (planar fractures), rather than as zones of dense PDF development. The latter were, on the TEM scale, observed only in the 60-GPa specimen.

5. Conclusion

Zircon (ZrSiO$_4$) single crystals, cut perpendicular to the c-axis, were experimentally shock-deformed at shock pressures of 20, 40, and 60 GPa. The main results of TEM analysis of these shocked samples can be summarized as follows:

1) Deformation in the 20-GPa sample, and partly in the 40-GPa sample, entails both brittle and plastic deformation. Brittle deformation involves thin, open cracks occurring mainly in {100} planes. They are interpreted as micro-cleavages as the result of shock-induced shear stresses produced during the compression stage. Plastic deformation is indicated by abundant screw dislocations in a characteristic glide configuration. The dominant glide systems are $<100>$<010>. The large density of dislocations at crack tips suggests that plastic deformation was initiated by the micro-cracking process.

2) PDFs are present in the 40- and 60-GPa samples. They consist of thin (about 10-nm) planar defects filled with amorphous material of zircon composition. The formation of PDFs probably takes place at the shock front.

3) In the 40-GPa sample, a fraction of the zircon is converted to a high-pressure phase having the scheelite crystal structure. The phase transformation is complete in the 60-GPa sample. This transformation is initiated in the {100} planes of zircon. The phase transformation is displacive (martensitic), and the crystallographic relationships are {100}$_s$ // {112}$_s$ and [001]$_s$ // <110>$_s$. The scheel-
ite-structure phase contains a high density of twins in the \{112\} planes. With regard to the shock process, PDF formation is clearly an earlier process than transformation to scheelite structure.

(4) The optically resolved planar features in zircon are tentatively explained as micro-cleavage.

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