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Quantitative characterization of plastic deformation of single diamond crystals: A high pressure high temperature (HPHT) experimental deformation study combined with electron backscatter diffraction (EBSD)

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ABSTRACT

We report the results of a high-pressure high-temperature (HPHT) experimental investigation into the deformation of diamonds using the D-DIA apparatus. Electron backscatter diffraction (EBSD) data confirm that well-defined 300–700 nm wide {111} slip lamellae are in fact deformation micro-twins with a 60° rotation around a <111> axis. Such twins formed at high confining pressures even without any apparatus-induced differential stress; mechanical anisotropy within the cell assembly was sufficient for their formation with very little subsequent lattice bending (<1° per 100 μm). When apparatus-induced differential stresses were applied to diamonds under HPHT conditions, deformation twin lamellae were generated, and continuous and discontinuous crystal lattice bending occurred (4–18° per 100 μm), including bending of the {111} twin lamellae. The {111}<011> slip system dominates as expected for the face-centred cubic (FCC) structure of diamond. Slip occurs on multiple {111} planes resulting in rotation around <112> axes. Deformation microstructure characteristics depend on the orientation of the principal stress axes and finite strain but are independent of confining pressure and nitrogen content. All of the uniaxially deformed samples took on a brown colour, irrespective of their initial nitrogen characteristics. This is in contrast to the two quasi-hydrostatic experiments, which retained their original colour (colourless for nitrogen free diamond, yellow for single substitutional nitrogen, Type Ib diamond) despite the formation of {111} twin lamellae. Comparison of our experimental data with those from two natural brown diamonds from Finsch mine (South Africa) shows the same activation of the dominant slip system. However, no deformation twin lamellae are present in the natural samples. This difference may be due to the lower strain rates experienced by the natural samples investigated. Our study shows the applicability and potential of this type of analysis to the investigation of plastic deformation of diamonds under mantle conditions.

1. Introduction

Diamonds, along with the mineral and fluid inclusions that they may carry, represent the deepest samples of the Earth's mantle that can be found at the surface [1]. Their economic and scientific importance means that they are one of the most intensively studied minerals. Diamond crystals show a range of different morphologies, growth mechanisms, colours and textures, all of which can affect their economic value. Some of these characteristics are interdependent, for example brown and pink colours in diamonds have long been recognized to be associated with plastic deformation [2]. Often, the brown or pink colour is only observed in lamellae parallel to the {111} planes while the bulk of the diamond is colourless [3]; this feature commonly is referred to as "graining".

As observed in other face-centred cubic (FCC) materials, the main slip system in diamond is {111} <110>. This means that the {111} planes are the active slip planes with movement in the <110> directions. In diamond, the {111} planes are also the twin planes. Twins in diamonds can be created during growth (seen in natural diamonds [4,5] and high-pressure high-temperature (HPHT) experiments [6]) or induced by deformation [7]. In deformation experiments performed on diamonds under vacuum at high temperature [8] as well as at high pressure and high temperature (HPHT; [9]), the {111} lamellae produced

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were identified as deformation twins. This occurrence of deformation twin lamellae was then confirmed in natural samples by Varma [10]. Despite this finding being criticised in a review by Orlov [11], recent transmission electron microscopy (TEM) work on both experimentally deformed [12] and naturally deformed diamonds [13] has confirmed the presence of these {111} deformation twin lamellae.

Traditionally, the primary indication that a diamond has been subject to plastic deformation has been the occurrence of macroscopically visible slip planes/deformation twin lamellae that occur parallel to {111} faces, as well as brown colouration. Only relatively recently has the quantification of deformation characteristics in diamonds, encompassing scales from nm to mm, becomes possible due to the development of the SEM-based electron backscatter diffraction analysis (EBSD) technique [14,15]. A significant benefit of EBSD analysis over TEM work is that it does not require the preparation of very thin (~5 μm thick) slices of material; EBSD simply requires a suitably polished surface. Once deformation can be quantified through EBSD analysis, relationships between deformation features and other optical and chemical characteristics (e.g. Cathodoluminescence (CL), Secondary Electron (SE) and birefringence imaging, Raman and infrared (IR) mapping) can be established, offering new avenues of data interpretation. CL is often imaged to observe variations in defect concentrations that can highlight a sample's growth stratigraphy [16,17] as well as any defects related to deformation i.e. slip planes [13]. SE imaging is restricted to showing surface topography and morphological variations that may be induced by deformation or subsequent damage, while birefringence is the result of strain-induced optical anomalies [18]. Raman mapping can be used to qualitatively identify strain in the diamond lattice [13,19,20], and IR mapping can resolve the spatial distribution of impurities, in particular nitrogen and its aggregation state [21–24].

There are obvious benefits in establishing causal links between characteristics that can be measured by different techniques. Furthermore, if we can experimentally deform diamonds at mantle conditions e.g. >4 GPa and >1200 °C, it will be possible to establish how diamond deforms under different P-T and strain-rate conditions. As in systematic studies conducted on other geological material and metals [25], such experiments can be combined with detailed analysis of rheological behaviour and the developing microstructures [12], to interpret the deformation and its links to the chemical history of the diamond. All of this will allow us to make inferences about Earth's otherwise inaccessible mantle.

An additional important implication of plastic deformation for diamond studies is the possible effect it can have on the rate of nitrogen aggregation. Presently, the rate at which nitrogen atoms aggregate with other nitrogen atoms is used to estimate either how long a diamond has resided in the mantle, or the temperature at which it has resided [26,27]. This technique must assume that the aggregation process occurs at a known rate. A common misconception is that plastic deformation simply increases the rate of nitrogen aggregation. However, HPHT experiments investigating the effects of microstructure on impurity diffusion in diamonds have shown that the relationship between deformation (and resultant microstructure) and the rate of nitrogen aggregation is unclear [12]. Byrne et al. [28] have presented a theory as to how plastic deformation could lead to the break up of B centres (4 nitrogen atoms surrounding a vacancy) and create a variety of N3 (N_3–V), H3 (N–V–N) and single nitrogen centres. Therefore use of the simple age/temperature relationship for nitrogen aggregation in diamond should be used with extreme caution, especially in samples that exhibit evidence of plastic deformation.

EBSD has been applied to studying polycrystalline synthetic diamond [29,30] but to our knowledge, it has not been applied to the quantitative investigation of plastic deformation in experimentally deformed diamond. Recently, a variety of deformation features in polycrystalline diamondite were recognised utilizing EBSD [31,32], emphasising that experimental data are needed to interpret the deformation structures seen in diamond and in diamond aggregates.

Here we report a pilot study, combining a new method of deforming diamonds under HPHT conditions in a deformation DIA (D-DIA, a modified cubic-anvil press [33]), and using EBSD to quantitatively analyse the deformation that has occurred. Deformation data are compared to a range of imaging techniques, including CL, SE and birefringence imaging using the MetriPol system [34]. For comparative purposes, two naturally deformed brown diamonds are analysed by these methods as well. The results show that the D-DIA technique can deform diamonds at temperatures and pressures relevant to nature, and demonstrate the usefulness of EBSD analysis for the quantitative investigation of plastic deformation in diamonds. The observed microstructures include deformation twinning, gradual crystal bending and continuous and discontinuous discrete high- and low-angle boundaries.

2. Samples

Seven single-crystal synthetic diamonds (provided by DTC Maidenhead) were used in the HPHT experiments described below (Table 1). The reason for using synthetic diamonds was to reduce the likelihood that the samples already contained any internal strain and/or plastic deformation. The lack of residual stress and strain was confirmed by birefringence imaging. Three samples (DD192, DD194 and DD197) were yellow Type Ib (containing 100–150 ppm single-substitutional, un-aggregated nitrogen), with their three sets of orthogonal faces parallel to {100}. The other four samples were colourless Type IIa (nominally nitrogen-free, i.e. <10 ppm). DD193, DD196 and DD198 have one pair of faces parallel to (100), and two sets of faces parallel to {110}. Sample DD195 had one pair of faces parallel to (111), one pair parallel to $(-1\bar{1}2)$ and the final pair parallel to $(1\bar{1}0)$. All seven samples initially were approximately 1 mm cubes.

Two natural samples have also been analysed to compare their characteristics with those generated during the HPHT experiments. Both are from the private collection of Dr H. Judith Milledge (UCL); they are brown diamonds from the Finsch mine, South Africa. FJM01, of rounded dodecahedral morphology, showed obvious growth layering on its surface, probably revealed by dissolution, while FJM02 appeared to be a broken fragment of a larger stone. Both samples are approximately 1 mm in size. Facets were mechanically polished on both samples

Table 1
Description of the samples prior to experiments and the conditions they were subjected to. The details of the crystals' orientation within the experimental assemblies are also provided.

Run #	Diamond type	Starting colour	P (GPa)	T (°C)	Strain rate (s^{-1})	Crystal faces Uniaxial stress applied to	Side crystal faces
DD192	Ib	Yellow	7.3	~1700	0	(100)	(010), (001)
DD193	II	Colourless	7.3	~1700	0	(100)	(011), $(0\bar{1}1)$
DD194	Ib	Yellow	7.3	~1700	0.000024	(100)	(011), $(0\bar{1}1)$
DD195	II	Colourless	7.3	~1800	0.000028	(110)	$(1\bar{1}1)$, $(1\bar{1}2)$
DD196	II	Colourless	5.1	~1800	0.000029	(100)	(011), $(0\bar{1}1)$
DD197	Ib	Yellow	5.1	~1800	0.000030	(100)	(010), (001)
DD198	II	Colourless	5.1	~1800	0.000057	(100)	(011), $(0\bar{1}1)$