Application of precession electron diffraction to the characterization of (021) twinning in pseudo-hexagonal coesite

Damien Jacob, Patrick Cordier, Jean-Paul Morniroli, and Hans-Peter Schertl

ABSTRACT

Precession electron diffraction is used to characterize a (021) twin observed in coesite. Due to the quasi-hexagonal dimensions of coesite (monoclinic space group C12/c1 with $\beta = 120.34^\circ$), indexing of conventional spot patterns is ambiguous and the twin law determination is impossible. With precession, spot intensities enable the absolute indexing of the patterns. The method we used is based on the analysis of the departure from hexagonal symmetry. This ensures that all possible pseudo-equivalent monoclinic orientations are taken into account for the indexing. The orientation relationships between adjacent parts of the twin are then characterized. The twin is described as a mirror along (021), which is consistent with original descriptions of twinning in synthetic coesite and a previous characterization performed using large-angle convergent-beam electron diffraction (LACBED).

Keywords: Coesite, twin, TEM, precession electron diffraction

INTRODUCTION

In a previous study (Jacob et al. 2008), we reported a (021) twin characterization in coesite using large-angle convergent-beam electron diffraction (LACBED). This technique was used to overcome the difficulties encountered with the interpretation of conventional electron diffraction patterns of coesite. Indeed, the monoclinic lattice of coesite exhibits a small symmetry departure from an "ideal" hexagonal lattice. As a result, many [uvw] zone-axis electron diffraction patterns look similar and cannot be unambiguously identified using conventional selected-area electron diffraction (SAED) or microdiffraction techniques. Therefore, the (021) twin (Sclar et al. 1962; Schertl et al. 2005) cannot be unequivocally characterized.

Recent developments in electron diffraction call for a reappraisal of the possibilities offered by spot patterns. Among them is the Vincent-Midgley (Vincent and Midgley 1994) precession electron diffraction (PED) technique, which recently became available on transmission electron microscopes due to hardware implementations. Given the possibility of measuring the integrated intensity of the diffracted beams, this technique was originally developed for electron crystallography applications (Gjønnes 1997; Berg et al. 1998; Olyenikov et al. 2007; Sinkler et al. 2007). It has been used for space group identification (Morniroli et al. 2007, 2008), structure determination (Owen et al. 2006; Kverneland et al. 2006; Weirich et al. 2006; Boulahya et al. 2007; Dorset et al. 2007; Dudka et al. 2007, 2008; Gemmi and Nicolopoulos 2007), measurement of Debye-Waller factors (Midgley et al. 1998) and chemical bonding characterization (Avilov et al. 2007; Ciston et al. 2008). In the present study, we use the intensity data provided by PED to propose an original characterization of a crystal defect. The method described in this paper is also suited to the general case of pseudo-merohedral twins occurring in crystals suffering from small symmetry departure, e.g., on LaGaO$_3$ perovskite (Ji et al. in prep).

EXPERIMENTAL METHODS

The sample

Coesite is a high-pressure polymorph of silica stable in the pressure range 2.5–9 GPa, which exhibits monoclinic symmetry with space group C12/c1. Cell parameters are $a = 0.71356$, $b = 1.23692$, and $c = 0.71736$ nm, $\beta = 120.34^\circ$ (Levien and Prewitt 1981). The twinned coesite investigated in this study comes from a fine-grained pyrope garnet rock collected at Parigi, Dora-Maira Massif, Western Alps, Italy (Chopin 1984; Schertl et al. 1991). Coesite grains were selected based on optical examination of 30 µm thick sections of the sample (an optical micrograph is presented in Fig. 1 of Jacob et al. 2008). Specimens were then drilled out and glued to a 3 mm diameter copper TEM grid and ion-milled to electron transparency at 5 kV with an incident beam angle of 15°. Finally, the samples were coated with a thin carbon layer to promote electron conduction.

Precession electron diffraction in the TEM

Applying the PED technique, the incident beam is scanned at a constant precession angle (ranging from 1 to 3°) around the optical axis, in combination with an opposite and synchronized descan of the transmitted and diffracted beams below the specimen (Vincent and Midgley 1994). During the precession movement, the reciprocal lattice nodes are thus swept through the Ewald sphere and integrated intensities over a large range of deviation parameter $\alpha$ around the Bragg orientation are collected. PED has the following main advantages: (1) the zone axis patterns are very symmetrical, even if the specimen zone axis is not exactly located along the optical axis; (2) the incident beam is never directed along the zone axis so that dynamical interactions are strongly reduced; (3) with large precession angles, a "two-beam" behavior is observed, which limits the multiple diffraction paths and allows the identification of the kinematical forbidden reflections; and (4) very small differences of intensity are visible.

TEM observations were carried out on a Philips CM30 microscope operated at 300 kV and equipped with a “Spinning Star” precession module from the Nanomegas Company. The sample is sensitive to electron irradiation, and the diffraction patterns were obtained with a low-dose parallel electron beam, using a 5