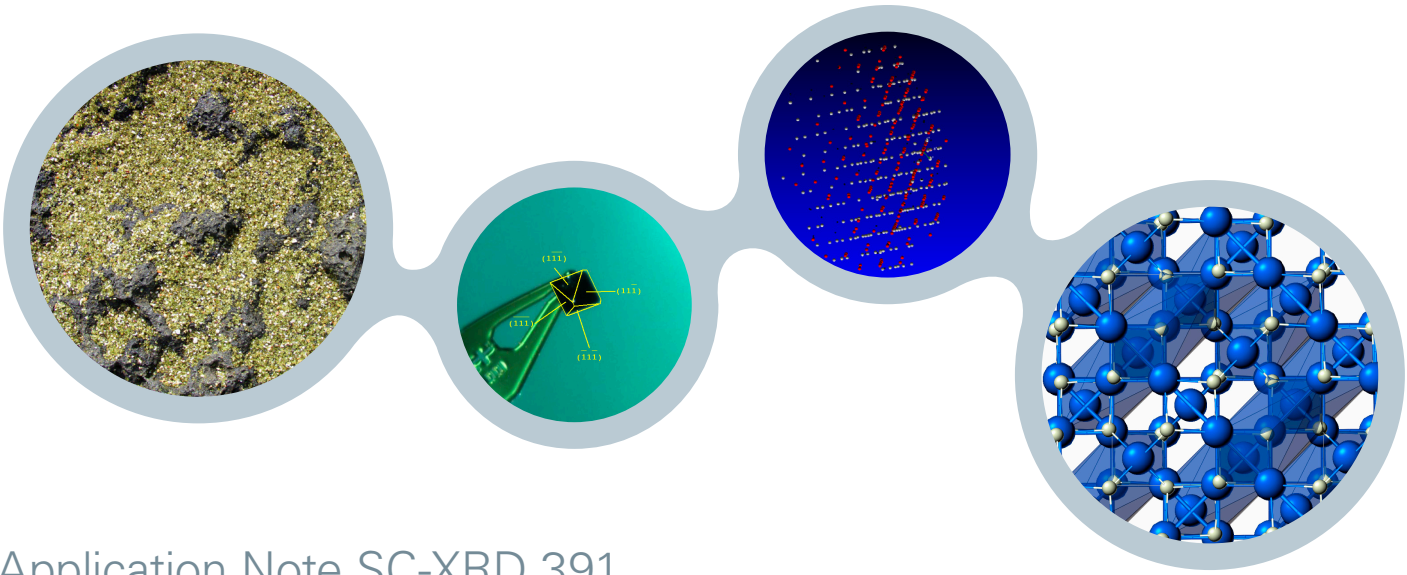

Application Note SC-XRD 391

Structure Determination of a Spinel Law (111) Contact-Twin of Chromite

Introduction

This application note describes the structure determination of a single crystal and a twinned chromite sample. Chromite forms in deep ultramafic magmas such as peridotites and is one of the first minerals to crystallize. Chromite is an iron chromium oxide mineral of the spinel group with the chemical composition $FeCr_2O_4$. Magnesium can substitute for iron in variable amounts as it forms a solid solution. Crystal shapes include octahedrons, often with dodecahedral faces modifying the edges of the octahedron to the point of rounding the crystal. Well-formed crystals are rare and chromite is usually found massive or granular. The samples investigated originate from olivine-rich green sands from a Hawaiian beach.

Crystal samples

The single crystal sample investigated was a small black octahedron with approximate dimensions of 0.25 × 0.25 × 0.25 mm. The twinned crystal examined was a contact twin of two crystals that share one face of an octahedron. The samples were mounted on Mitegen Micromounts using a thin film of Paratone oil as adhesive. Twins are regular aggregates consisting of individual crystals of the same species joined together in a defined mutual orientation. For the twin investigated, each crystal has the approximate dimensions of 0.25 × 0.25 × 0.25 mm, similar to the single crystal sample. The face that is shared between the crystals, the twin plane, is parallel to the octahedron face (111) (Figure 1), and the twin is formed by a rotation of one of the crystals about a triad axis. This type of twinning is referred to as the "Spinel Law" because it is most commonly seen in spinel crystals. Figure 2 and Figure 3 show models for an octahedral single crystal and a (111) contact twin.

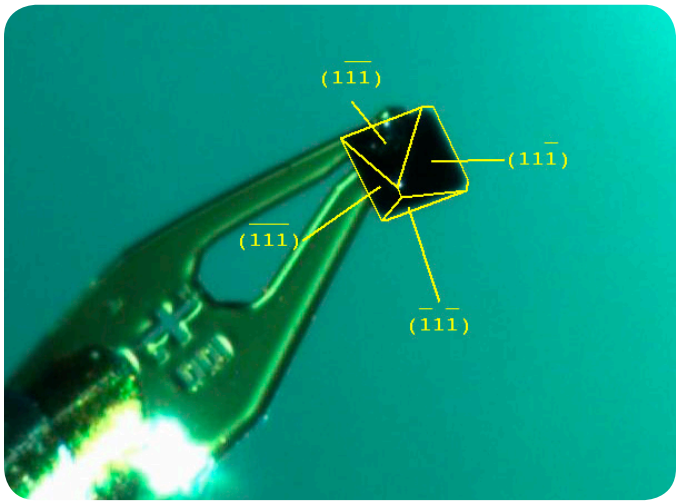

Figure 1. (111) faces of the octahedral chromite crystal.

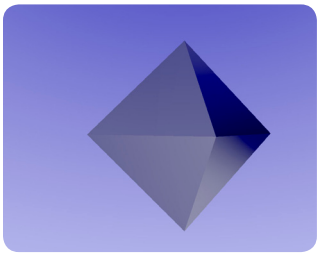

Figure 2. Model of an octahedral single crystal.

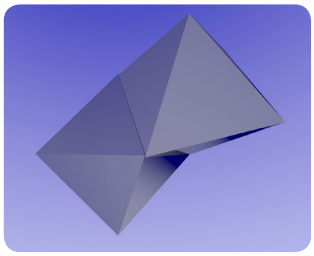

Figure 3. Model of a (111) contact twin.

Chromite single crystal

The structure of chromite was determined in a straightforward experiment from a single crystal to provide a reference data set for the subsequent crystallographic experiment with the twinned crystal. Data of the chromite single crystal were acquired using APEX2 software on a D8 QUEST diffraction system equipped with a fine-focus sealed-tube Mo X-ray source, a TRIUMPH monochromator, and a PHOTON 100 detector. 7-fold redundant data were collected to 0.6 Å in 12 min. The sample crystallizes in the cubic space group Fd-3m with a= 8.3217(9)Å crystal faces were indexed to confirm the index (111) for the contact face of the twin (Figure 1). The structure refines as $Fe_{0.79}Mg_{0.21}Cr_2O_4$ with a reliability criterion R1 of 2.30%. Iron content was determined by simultaneous refinement of the Fe and Mg site occupancy factors, while constraining the positional parameters and anisotropic displacement factors of the Fe and Mg to be equal. Table 1 lists the most important reliability criteria and Figure 4 shows a representation of the chromite structure.

Chromite single-crystal structure data	
Formula	$Fe_{0.79}Mg_{0.21}Cr_2O_4$
Rint	2.49%
Rsym	1.87%
Unique data observed	83
Unique data all	87
Max. resolution	72.56°, 0.6Å
R1	2.30%
wR2	5.95%

Table 1. Quality criteria for the chromite single crystal structure.

Chromite contact-twin crystal

The structure of chromite from a twinned sample was determined in a similar experiment to the structure determination from a single crystal described above. Data of the chromite twinned crystal were acquired using the same D8 QUEST configuration as described above. 7-fold redundant data were also collected to 0.6 Å in 12 min. After manually separating reflections using the reciprocal lattice viewer RLATT, subsequent indexing gave two orientation matrices, each describing one twin domain. This result was confirmed with the automated least-squares twin indexing routine of CELL_NOW. The second domain was found to be rotated 56.091° from the first, resulting in nearly perfect Spinel twinning. Data were integrated using SAINT, which provides twinning algorithms that process both domains simultaneously and employ spot profiles to determine reflection overlap. Data scaling and absorption correction were performed using TWINABS, which also generated the intensity data files for structure solution and refinement with SHELXTL.

Chromite structure

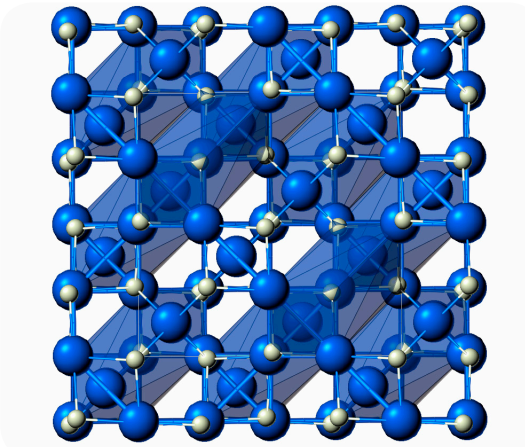

Figure 4. Cubic spinel structure of chromite

The sample crystallizes in the cubic space group Fd-3m with a= 8.3056 (6) Å. Treating the crystal as a twinned sample and de-convoluting the twinned diffraction pattern yields a structure that has similar high quality as the structure derived from a single crystal. The structure refines as $Fe_{0.75}Mg_{0.25}Cr_2O_4$ with a reliability criterion R1 of 2.05%. Table 2 lists the most important reliability criteria for the twinned chromite structure.

Chromite twinned-crystal structure data	
Formula	$Fe_{0.75}Mg_{0.25}Cr_2O_4$
Rint	n/a
Rsym	1.37%
Unique data observed	82
Unique data all	85
Max. resolution	72.56°, 0.6Å
R1	2.05%
wR2	5.30%

Table 2. Quality criteria for the chromite twinned crystal structure.

Unit cell determination

APEX2 software provides a series of tools for unit-cell determination of twinned crystals. The *Reciprocal Lattice Viewer* plug-in allows not only the display of reciprocal lattices but also their manipulation and subsequent indexing using difference vector and FFT methods. Linear least-squares methods, as employed by CELL_NOW, use a brute-force algorithm for automated indexing and the *Compare Unit Cell* plug-in can compute the twin law by comparing the individual twin component unit cells. (Table 3).

Spinel twin law "60°" rotation about (111)	
Rotation angle (°):	56.091
Rotation vector (reciprocal cell):	1.00 1.00 1.00
Rotation vector (direct cell):	1.00 1.00 1.00
Unit cell relationship:	a′ = +1 × a b′ = +1 × c c′ = -1 × b
Superposition matrix:	H′ = +0.706×H+0.627×K-0.331× L K′ = -0.332×H+0.705× K+0.627× L L′ = +0.626×H-0.333×K+0.705×L

Table 3. Rotation vectors, unit cell relationship and superposition matrix for the two chromite twin domains.

Visual indexing using the *Reciprocal Lattice Viewer* plug-in

The Reciprocal Lattice Viewer plug-in allows users to display in a 3-dimensional space the reflections present in the reciprocal lattices, as well as to manipulate and edit these reflections into two or more lattices. By rotating the array of reciprocal lattice points, it is easy to visualize patterns of ordered lines and interpenetrating lattices that can be difficult for computer algorithms to recognize. Lattice overlay tools can be used to mark lines and separate groups of reflections into different color bins for subsequent indexing. Figure 5 shows the overlay tool selecting one of the twin domains.

Least-squares indexing

This is a brute-force algorithm which can index multicomponent nonmerohedral twins. Multiple random real-space starting vectors with lengths set between user-input limits are refined by iterative linear least-squares refinement. A weighting scheme strongly down-weights reflections that do not fit well and concentrates the refinement to the better-fitting reflections, which in general will belong to the same twin domain. The reflections that do not fit the first twin domain can be used to search for additional domains. The cell for the first domain is rotated to give a good fit to as many of these reflections as possible. The rotation required (often 180° about a real or reciprocal axis) provides a description of the type of twinning. After assigning reflections to the second domain, the reflections that do not fit either domain may be used to search for additional domains in the same way.

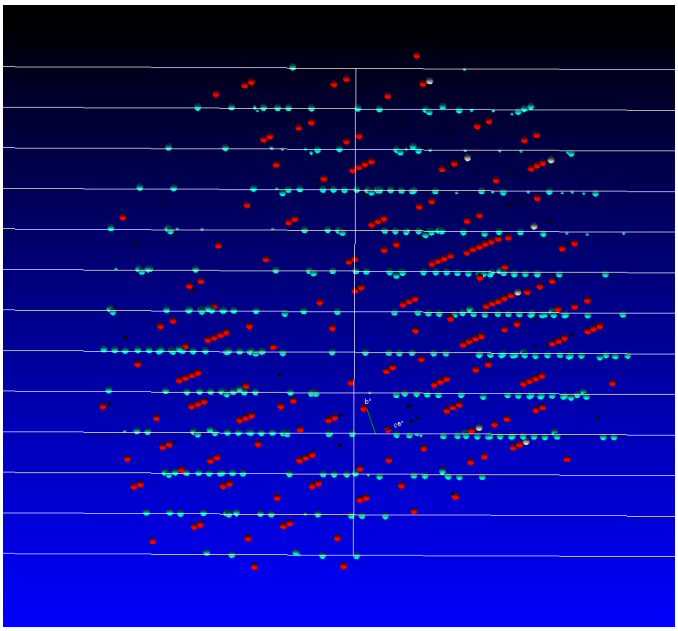

Figure 5. Reciprocal lattice viewer overlay tool for separation of reflections from different domains.

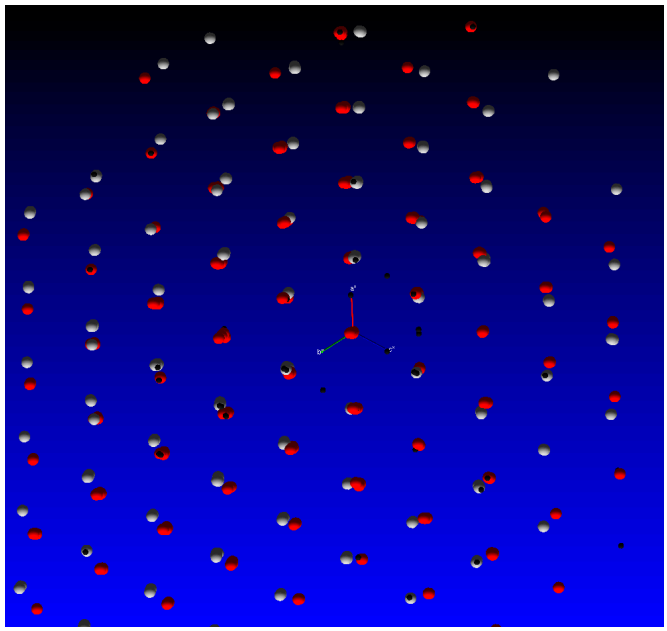

Figure 6. View along reciprocal vector 1 1 1 reveals the 56° rotation between the twin domains.

Data integration

Data integration of a twinned crystal is easy and straightforward. If more than one orientation matrix is provided, the integration engine SAINT will automatically switch to a twin-integration mode. SAINT allows integration of up to 8 domains simultaneously. SAINT uses a profile-based twin-pairing method to determine when spots start to overlap and multi-component spot overlap is computed based on overlap of the model profiles. In the case of twin overlaps, SAINT estimates the intensities of individual spot components and writes them to the output reflection file in a HKLF 5 style format that can be scaled and corrected for absorption with TWINABS. The intensity esds are equal for each spot component and correspond to the esd of the aggregate intensity sum. The additional intensity information has been added to increase the information available for scaling and absorption correction with TWINABS and subsequent structure solution and refinement using SHELXTL. SAINT allows one of two types of inter-component constraints to be applied in twin refinements, to support cases where one or more components exhibit much weaker diffraction than the first component. The integration GUI provides extensive graphical feedback for each twin component as well as overall quality of the data integration. Color-coded spot position overlays can be displayed to follow the data integration process. (Figure 8)

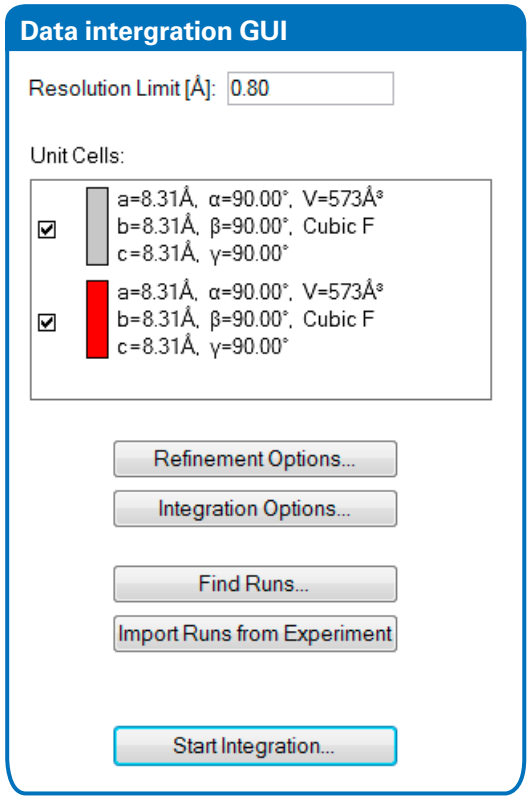

Figure 7. Two twin domains for data integration

Scaling and absorption correction

The raw data file generated during data integration needs further processing for deconvolution of overlapping reflection. TWINABS uses information from non-overlapping reflections of the multicomponent file to determine the absorption profile and parameters for data scaling as well as correction of the intensities standard uncertainties. TWINABS employs a multiscan method using information from many sets of equivalent reflections analyzed. The program also produces an HKLF 4 file for space group determination and structure solution as well as an HKLF 5 file for structure refinement.

Summary

With the D8 QUEST and D8 VENTURE, nonmerohedral twins can presently be handled very efficiently, and the data derived from these samples is of the same high quality that researchers have come to expect from Bruker's state-of-the-art diffraction instrumentation. The D8 QUEST and D8 VENTURE solutions for chemical crystallography, and the APEX2 software suite are easy to use, and the sophisticated hardware and underlying algorithms provide powerful tools to crystallographers for tackling crystallographically challenging samples.

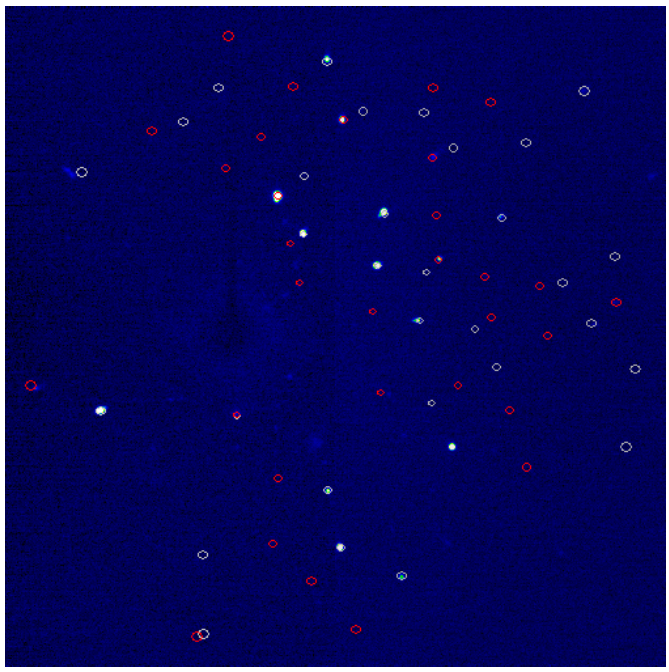

Figure 8. Color-coded spot position overlay for each twin domain.

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