

Structure refinement using precession electron diffraction tomography and dynamical calculations: application to pyroxene

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1. INTRODUCTION

The precession electron diffraction (PED) technique [1] has been originally developed for structure determination at a submicrometer scale in a transmission electron microscope (TEM). The resulting intensities keep dynamical in nature, due to electron multiple scattering, but are more closely correlated with the structure factor values with respect to the non-precessed intensities, which is crucial for structure solution and refinement [2]. Since, many structures have been solved using PED, recently combined with the tomographic acquisition of 3D electron diffraction data (PEDT) [3]. Even more recently, a full structure refinement method based on PEDT data and dynamical calculations of diffracted intensities has been successfully proposed [4]. We present here some results concerning the application of this new method to the refinement of (Mg,Fe)SiO₃ pyroxene structures in order to determine the Fe²⁺ and Mg ordering on specific mixed sites of these structures of mineralogical interest.

2. RESULTS

2.1 Samples and instrumentation

Natural pyroxene monocrystalline grains of various origins and compositions have been selected and studied by electron microprobe for chemical composition analysis and X-ray diffraction for structure refinements at the grain scale (100-300 μ m in size). Some samples have also been heat-treated (24 h at 1000°C followed by a rapid quench) in order to intentionally induce some structural disorder associated with Fe²⁺ and Mg occupancy variations on specific M1 and M2 sites of the structures. The structures deduced from XRD refinement will serve as models for comparison with the much more local results obtained using TEM electron diffraction data. TEM samples have been extracted from the original single grains by Focused Ion Beam at the IEMN (D. Toadec, IEMN, UMR CNRS 8520 - Université Lille 1). Precession electron diffraction data have been acquired on a LaB₆ FEI Tecnai G2 operated at 200 kV and equipped with a Nanomegas Digistar precession system.

2.2 Method

The method is precisely described in [4]. It is based on the acquisition of series of precessed (1-2° precession angle) diffraction patterns acquired for various tilt angles of the samples as currently done in electron tomography (+/- 45 to 60°, by step of 1°). The 3D reciprocal space is then reconstructed (Fig. 1) and experimental I_{hkl} intensities are integrated using the softwares PETS and JANA2006. From the I_{hkl} data set, the structure is solved, using conventional X-ray methods based on the kinematical approximation implemented in JANA2006, in order to obtain a first reliable structure model. The model is finally accurately refined (atomic position and occupancies) using least-squares methods based on the comparison of experimental intensities with calculated ones using the dynamical theory. In this work, we will describe the influence of the various experimental and computational parameters on the accuracy and precision of the refinement results.

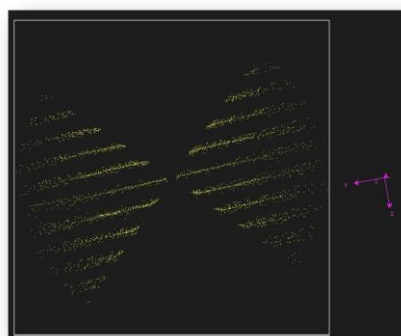


Figure 1. 3D reconstruction of the portion of the reciprocal space sampled during the tomographic acquisition of electron diffraction data. Heat-treated orthopyroxene sample, $\pm 45^\circ$ tilt series.

2.3 Preliminary results and perspectives

In a previous work, we had already shown that electron diffraction data set acquired on a single zone axis orientation could be efficiently used to refine occupancies of Fe^{2+} and Mg^{2+} cations in a model orthopyroxene structure [5]. The sensitivity of the method was clearly sufficient to distinguish between samples with various ordering states and cooling histories. Here, no previous knowledge of the structure is required since the model can be directly deduced from the 3D electron data set itself, containing about 1000 reflections. Refinement of the site occupancies and positions against dynamical calculations of diffracted intensities then clearly enables the retrieval of a more accurate structure, with standard deviations on positions and occupancies about only three times larger than those usually obtained with XRD. Despite these larger uncertainties, the PEDT method coupled to the dynamical refinement of intensities should enable the routine use of electron diffraction data for applications in the field of mineralogy and the use of structures of submicrons grains as geothermometers for the determination of the cooling history of the hosting rock. Applications are also numerous in other material sciences domains where accurate structure determination have to be achieved at a very local scale, as it is the case for functional applications of oxides deposited as thin films on substrates where other conventional structural methods are not adapted [6].

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