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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Vacancy Ordering in Mullite - Analysis of the Incumensurate Modulation and Diffuse Scattering	**Experiment number**: HC 3053
Beamline: BM01	**Date of experiment**: from: 02.03.2017 to: 03.03.2017	**Date of report**: 28.03.2018
Shifts: 3	**Local contact(s)**: Dr. Dmitry Chernyshov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Paul B. Klar*, **Gotzon Madariaga***

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Report:

Before our experiments at BM01 little was known about the ordering phenomena in mullite, in which Al/Si and vacancy ordering is present. Our laboratory experiments were not able to detect diffuse scattering and only sharp satellite reflections were visible. The resulting model is a fully ordered model, but requires the presence of a disordered phase.

9 different samples from 4 sample batches were measured at BM01 (single crystal X-ray diffraction, optimized for diffuse scattering and structure solution). The total measurement time of successful experiments was about 13 hours of the 24 available hours. The rest of the time was used for sample preparation, alignment, test measurements and measurements of low quality samples (e.g. poly crystalline).

The new measurements resulted in a new model for the modulated crystal structure of mullite and better understanding of it. First, the presence of diffuse scattering could clarify our main question concerning the disordered phase. On the other hand, the absence of higher order satellites shows that our ordered model does not correctly describe the structure of the measured samples.

Data reductions (CrysAlis PRO) were carried out for 4 measurements and lead to the development of a new superspace model. The different refinements are basically the same, but they exhibit different modulation amplitudes, which is interpreted in terms of different degrees of ordering. It was known before, that ordered and disordered mullite exists, but our measurements show that a range of degrees of ordering exist. Our previous, ordered model is in full agreement with the new, disordered model, in the sense that the ordered model represents the highest degree of ordering.

Due to the great resolution and quality of the measurements, we were able to develop a new approach to define Al/Si ordering from the displacive modulation and the comparison of tetrahedra volumes with DFT calculations. The observed, average volume agrees perfectly with the expected value, and thus the modulation allows to define the Al/Si ordering on the tetrahedra sites.
Thanks to the measurements at BM01 we could develop a consistent superspace model for a crystal structure, that is already investigated for about 50 years. The puzzle of vacancy and Al/Si ordering in mullite now for the first time allows to recognize the full picture.

We highly appreciate the given beamtime. We especially want to thank the beamline scientist Dr. Dmitry Chernyshov. It is also thanks to him and his maintenance of the beamline that our measurements were successful. In addition we thank the ESRF for financial support and a smooth organization of the stay at the synchrotron and at the guest house.

Parts of the measurements were presented as oral presentation at the following conferences:

Mullite – Towards a Unified Superspace Model (2017), presented as talk
P. B. Klar, N. de la Pinta, G. A. Lopez, I. Etxebarria, T. Brezcewski and G. Madariaga,
24th Congress and General Assembly of the International Union of Crystallography,
Hyderabad, India, August 2017
Acta Cryst A**73**, C1121
Mullite Al/Si ordering in superspace revealed by DFT (2018), presented as talk
P. B. Klar, I. Etxebarria and G. Madariaga, 26th Annual Meeting of the German
Crystallographic Association, Essen, Germany, March 2018

An article was submitted to IUCrJ at the end of February 2018 and is currently under review. The abstract of the submitted article is the following:

Synchrotron single crystal X-ray diffraction revealed diffuse scattering alongside sharp satellite reflections for different samples of mullite ($Al_{4+2x}Si_{2-2x}O_{10-x}$). Structural models were developed in (3+1)d superspace that account for vacancy ordering and Al/Si ordering based on harmonic modulation functions. A constraint scheme is presented which explains the crystal chemical relationships between the split sites of the average structure. The modulation amplitudes of the refinements differ significantly by a factor of ~3, which is explained in terms of different degrees of ordering, i.e. vacancies follow the same ordering principle in all samples, but to different extents. A new approach is applied for the first time to determine the Al/Si ordering by combining density functional theory with the modulated volumes of the tetrahedra. The presence of Si-Si diclusters indicate that the mineral classification of mullite needs to be reviewed. A description of the crystal structure of mullite must both consider the chemical composition and the degree of ordering. This is of special importance for applications as advanced ceramic, because the physical properties depend on the intrinsic structure of mullite.

Ongoing work focuses on the diffuse scattering and we believe that at least two papers will result from the results obtained at BM01.