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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:** High-temperature crystallographic behavior of In_2Se_3	**Experiment number**: **HC-3838**
Beamline: ID22	**Date of experiment**: from: 22.08.2018 to: 26.08.2018	**Date of report**:
Shifts: 6	**Local contact(s)**: Mauro Coduri	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In our proposal, we showed that the phase-transition behavior and the crystal structures of In_2Se_3 are not fully understood. Literature phase-transition temperatures show a large spread, and most high temperature crystal structures were not refined.

During our measurements at beam line ID22 at the ESRF, we successfully measured the high-temperature behavior of three different In_2Se_3 polymorphs that are stable or metastable at room temperature: 2H-α, 3R-α and γ. We used a standard experimental setup for high-temperature diffraction measurements with a hot air blower as proposed.

Starting from γ-In_2Se_3, we could observe a phase-transition into δ-In_2Se_3 at 575 °C, which is stable up to at least 800 °C. We used a diffraction pattern at 700 °C to solve and refine the crystal structure of δ-In_2Se_3. It crystallizes in space group $P\bar{3}m1$ with Se–In–Se–In–Se layers (In1: 2*d*, *z* = 0.8010(3), Se1: 1*a*, and Se2: 2*d*, *z* = 0.3353(4)). All In atoms are coordinated octahedrally by six Se atoms. The crystal structure is polytypic to 3R-β-In_2Se_3 with the Bi_2Te_3 structure type, but with a different translational symmetry along *c*. The crystal structure of δ-In_2Se_3 is projected in Figure 1. To best of our knowledge, this is the first time that atomic positions of this phase were refined.

Starting from 3R-α-In_2Se_3, we observed a phase-transition into 3R-β-In_2Se_3 at 175 °C. Here, the tetrahedrally coordinated In atom changes into an octahedral coordination (see Figure 1). Using the high-resolution diffraction data, we were able to refine the crystal structure of 3R-β-In_2Se_3 and determine atomic positions. By heating up 3R-β further, it transforms into γ-In_2Se_3 starting at 350 °C. The transition showed a very broad temperature range and was not completed until heating to 525 °C. We know from previous experiments that tempering

In_2Se_3 at 400 °C leads to phase-pure γ-In_2Se_3. Therefore, the transition is rather kinetically than thermodynamically controlled which might explain the varying transition temperatures reported in the literature. Upon further heating the sample transforms to δ-In_2Se_3 at 575 °C, which is in line with the transition temperature which we observed for the first sample.

In our proposal we showed that we were able to develop a structure model for 2H-α-In_2Se_3 from electron microscopy, DFT calculations and in-house XRD measurements. With the help of the high-resolution XRD measurements from ID22, we were able to refine the atomic positions of 2H-α-In_2Se_3 for the first time. It consists of five different atomic sites and forms Se–In–Se–In–Se layers (see Figure 1) within space group $P6_3mc$. By heating 2H-α-In_2Se_3, a phase transition is observed at 200 °C. This phase above 200 °C shows a hexagonal lattice. By considering the transformation between 3R-α and 3R-β (coordination change of one In atom) we assumed the same transition for 2H-α-In_2Se_3 and developed a structure model consisting of Se–In–Se–In–Se layers with octahedrally coordinated In atoms (see Figure 1). We refined the model with the XRD data at 250 °C. To best of our knowledge, the phase was never reported before.

The experimental setup of measuring in sealed capillaries results in a strong temperature gradient, since only a small part of the capillary is heated with the hot air blower. At high temperatures (above 800 °C) we observed significant sublimation of In_2Se_3 within the capillaries. This probably resulted in an unfortunate compositional change. Therefore, the XRD measurements during the cooling process could not be reproduced, for trivial reasons. An experimental setup where the entire sample container is heated homogeneously will be necessary to arrive at reproducible results during the cooling process.

The results we could make in the measurements during the heating steps already significantly improve the understanding of the crystallization behavior of In_2Se_3. A manuscript regarding the results is in preparation.

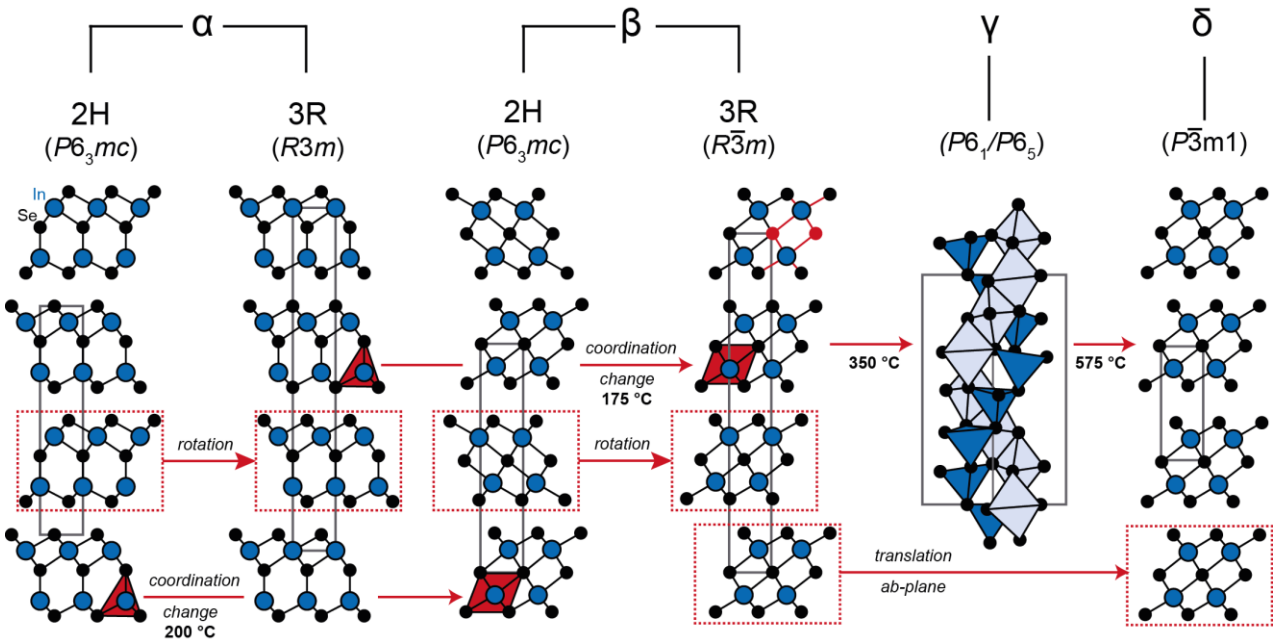

Figure 1: Projection of the refined crystal structures of the different In_2Se_3 polymorphs. Transition temperatures and symmetry operations between selected polymorphs are indicated.