



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://www.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.



	Experiment title: Higher manganese silicides - perspective energy-harvesting thermoelectric materials	Experiment number: MA-2322
Beamline: ID22	Date of experiment: from: 24 July 2014 to: 27 July 2014	Date of report:
Shifts: 10	Local contact(s): Andy Fitch	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Anastasiia Prytyliak* David Berthebaud* Dao Y Nhi Truong*		

Report:

1. Background and motivation

The objectives of the ThermoMag Integrated Project within the EU 7th Framework Program is to develop and deliver new energy harvesting thermoelectric (TE) materials based on abundant and ecologically friendly elements, for example magnesium silicide Mg_2Si and Higher Manganese Silicides (HMS) $MnSi_\gamma$ ($\gamma = 1.71-1.75$). The band gap and density of states near Fermi level, which are responsible for thermoelectric properties of HMS, depend on their actual compositions, which were rarely identified in previous reports due to lacking of clear evidences from lab-scale characterization methods. The experiments at ESRF will help us to indicate the compositional ratios of different HMS-based materials, and understand their structural evolutions with elevated temperatures and various dopants.

2. Results

Fourteen samples were measured during the experiment with different temperature cycles. The heating and cooling programs of the later samples were selected basing on the preliminary data analysis of the previous ones. For the high temperature experiments, the powders were contained in borosilicate glass

capillaries with 1 mm in diameter prepared under helium atmosphere to avoid oxidation, the heating up process was provided by hot air blower.

High resolution X-ray diffraction patterns obtained from synchrotron radiations have precisely shown the peak positions of different HMS compounds, as well as small amounts of present impurities, usually hindered by the high background of conventional X-ray instruments due to the existence of manganese. An example was given in Figure 1, showing the major phase of HMS and a tiny peak of Si (estimated to be less than 1 at.-%). It is noticed that no significant chemical decompositions are observed over the whole temperature range. Le Bail refinements are performed by fitting the experimental patterns with the theoretical ones of the sublattices of manganese and silicon to obtain the cell parameters and the ratios $c_{\text{Mn}}/c_{\text{Si}}$ of these sublattices. These ratios help to predict the compositions of different HMS compounds. The stoichiometry is identified to correspond to $\text{Mn}_{15}\text{Si}_{26}$ at room temperature for all the investigated samples.

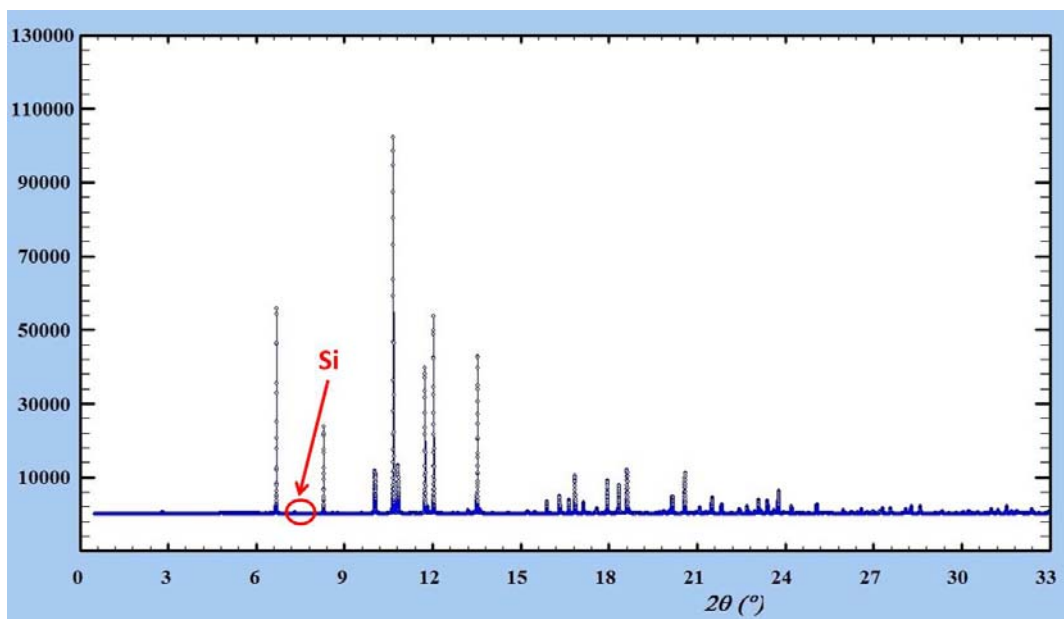


Figure 1: Typical diffraction pattern recorded from $\text{MnSi}_{1.75}$ stoichiometry with a tiny peak of silicon (estimated to be less than 1 at.-%)

The manganese and silicon subcells are expanded with increasing temperatures due to thermal agitations at atomic levels with different magnitudes, leading to changing the $c_{\text{Mn}}/c_{\text{Si}}$ ratios. The modifications depend on the nominal compositions of the materials. Generally, this ratio increases with elevated temperatures up to a saturated value of approximately 1.736, then decrease with further heating for the samples containing only manganese and silicon, as illustrated in Figure 2 for the sample with nominal compositions of $\text{MnSi}_{1.75}$. The saturating temperatures are less than 700°C for all the samples and decrease with increasing the amount of silicon. Unfortunately, the cooling cycle show poor reproducibility of these ratios; the reason is suggested to be the presence of impurities (manganese monosilicide MnSi or silicon). The phase transitions are predicted to happened after the saturating points due to intolerant disturbance of the structures at high temperature.

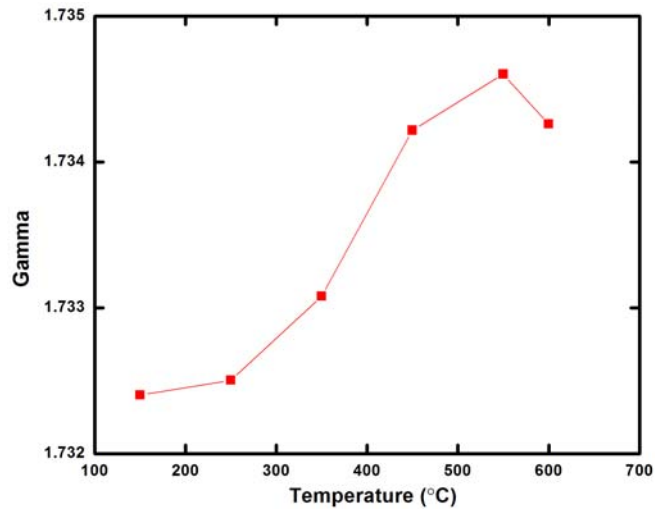


Figure 2: Temperaturational revolution of γ (MnSi_γ) obtained from profile matching the synchrotron patterns with the sublattices of manganese and silicon for the sample with nominal compositions of $\text{MnSi}_{1.75}$

Due to limited time for experiments, the doped samples were either measured only at room temperature or heated up to less than 700°C . Germanium, aluminum, and chromium are inserted into the structure of HMS, while molybdenum disilicide MoSi_2 is identified as impurity due to the large size of molybdenum. At room temperature, the predicted compound for Ge-doped HMS is $\text{Mn}_{11}\text{Si}_{19}$, and for the others still is $\text{Mn}_{15}\text{Si}_{26}$. The temperature dependence shows clear dependence on the doping types. With germanium (Figure 3 (a)) and chromium as dopants, the ratio increases with increasing temperature, but has not reached the saturated point yet in this temperature range. On the other hand, the Al-doped HMS (Figure 3 (b)) show a decreasing trend of this ratio with increasing temperature.

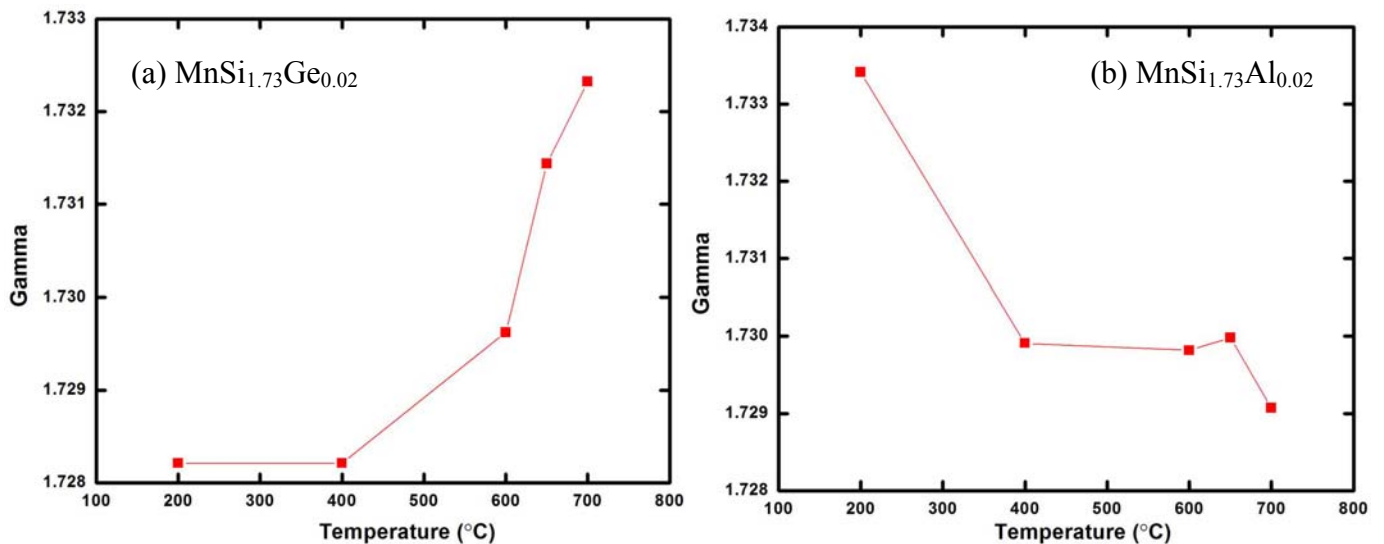


Figure 3: Temperaturational revolution of γ (MnSi_γ) obtained from profile matching the synchrotron patterns with the sublattices of manganese and silicon for the samples with nominal compositions of (a) $\text{MnSi}_{1.73}\text{Ge}_{0.02}$ and (b) $\text{MnSi}_{1.73}\text{Al}_{0.02}$

3. Conclusions

The experiments allowed us to predict the actual compositions of HMS, and the dependences on temperature and dopants. The achieved results help to optimize the synthesis and measurement conditions for future experiments to improve the thermoelectric performance of HMS-based materials.