

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 are to develop and deliver new energy harvesting thermoelectric 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 the Fermi level, which are responsible for thermoelectric properties of HMS, depend on their actual compositions. Unfortunately, the precise stoichiometry was rarely identified in previous reports due to the lack of clear evidences from lab-scale characterization methods. The experiments at ESRF were performed in order to help us to indicate the compositional ratios (γ) of different HMS-based materials together with various dopants and understand their structural evolutions at elevated temperatures.

2. Results

Fourteen samples were analyzed during the experiment under different thermal cycles. The heating and cooling programs of the later samples were selected based 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 the oxidation, the heating 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 is given at Fig. 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 were 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.

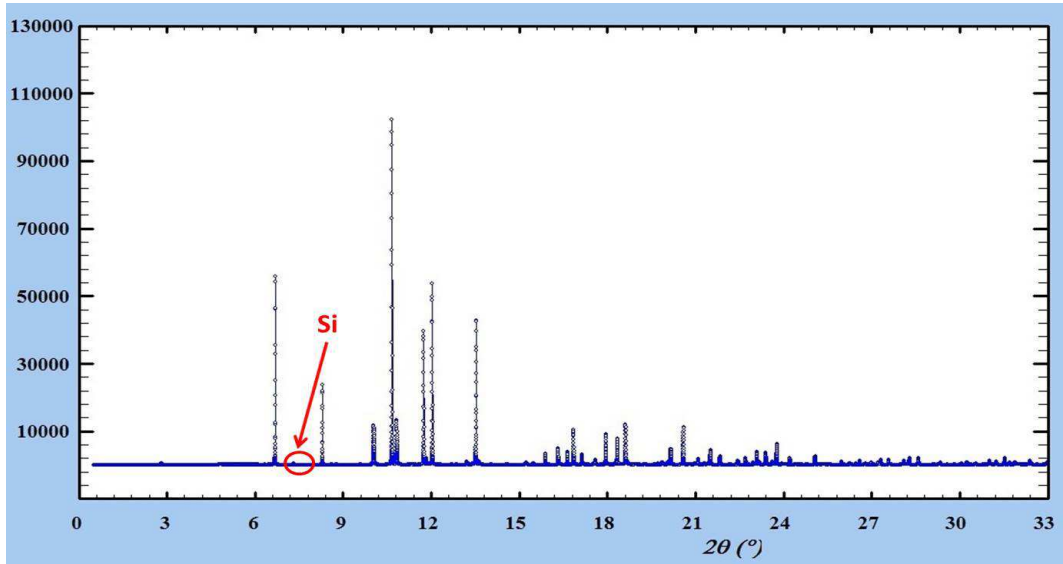


Figure 1: Typical diffraction pattern recorded from $\text{MnSi}_{1.75}$ stoichiometry with a tiny peak of silicon (estimated to be less than 1 at.-%)

The manganese and silicon subcells are expanded with increasing temperatures due to thermal agitations at atomic levels with different magnitudes, leading to the change in $c_{\text{Mn}}/c_{\text{Si}}$ 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 at Fig. 2 for the sample with nominal composition of $\text{MnSi}_{1.75}$.

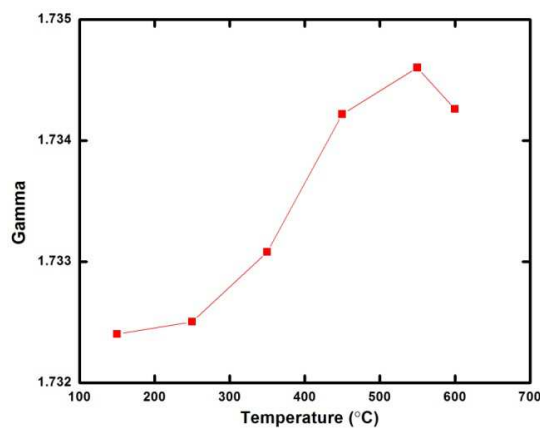


Figure 2: Temperature dependence of γ (MnSi_γ) obtained from profile matching of the synchrotron patterns with the sublattices of manganese and silicon for the sample with nominal compositions of $\text{MnSi}_{1.75}$

The saturation temperatures are less than 700°C for all the samples and decrease with increasing of silicon amount. Unfortunately, the cooling cycle have shown poor reproducibility of these ratios; the reasons are suggested to be either the presence of impurities (manganese monosilicide MnSi or silicon), or the irreversibility of the transformation. The phase transitions are predicted to happen after the saturation points due to intolerant disturbance of the structures at high temperature.

Due to the 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 appeared to be inserted into the structure of HMS, while molybdenum disilicide MoSi₂ is identified as impurity due to the large size of molybdenum. At room temperature, the predicted composition for Ge-doped HMS was Mn₁₁Si₁₉, and for the others - still Mn₁₅Si₂₆. The evolution with the temperature have shown clear dependence on the doping types. In the cases of germanium (Fig.3 a) and chromium dopants, the ratio increases with the temperature growth, but do not reach the saturation point in the temperature range. On the other hand, the Al-doped HMS (Fig. 3 b) have shown a trend to decrease this ratio with temperature growth.

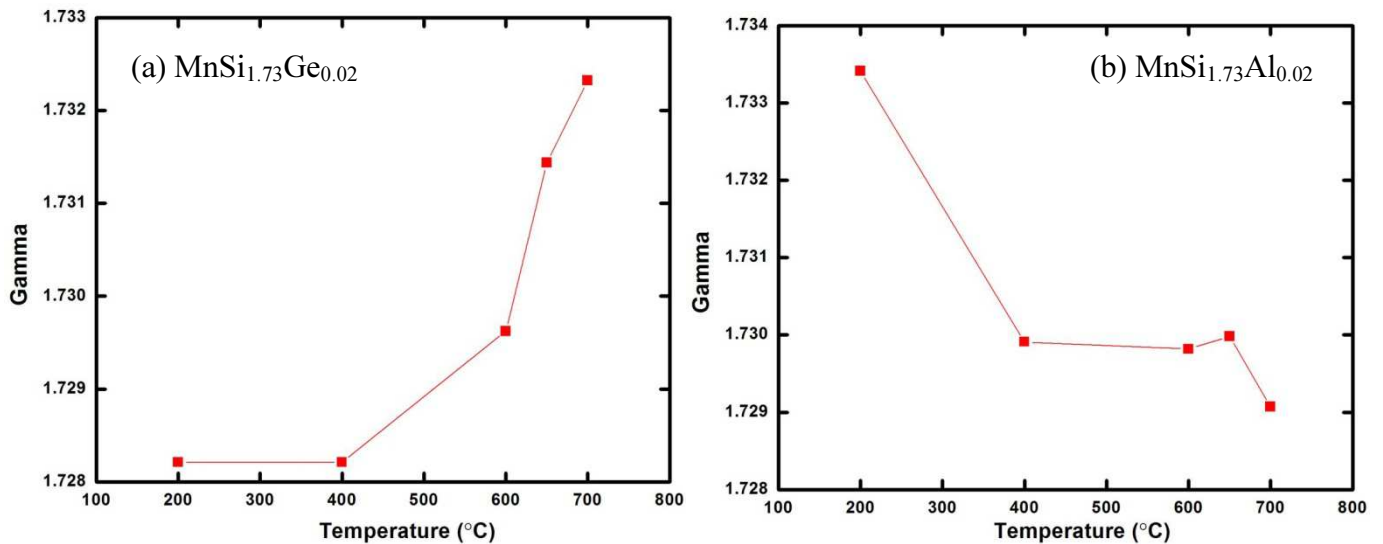


Figure 3: Temperature dependence of γ (MnSi _{γ}) obtained from profile matching the synchrotron patterns with the sublattices of manganese and silicon for the samples with nominal compositions of (a) MnSi_{1.73}Ge_{0.02} and (b) MnSi_{1.73}Al_{0.02}

3. Conclusions

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