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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:** In-situ study of phase evolution with temperature in selected energy-harvesting $Mg_2Si_{(1-x)}Sn_x$ based thermoelectrics	**Experiment number**: MA-2041
Beamline: ID 15 A	**Date of experiment**: from: 1 December 2013 to: 4 December 2013	**Date of report**: 13.07.2014
Shifts: 6	**Local contact(s)**: Mario Scheel	*Received at ESRF:*

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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 3D nano-structured bulk Mg_2Si solid solutions. The goal of the study was to shed lights on the relationship between microstructural evolution and physical properties of the most promising thermoelectric materials, to clarify the role of dopants in the development of phases and establish the link between temperature - phase formation, growth and dissolution – and Seebeck coefficient. The experiment was expected to help us to identify the preferential segregation sites of dopants (grain boundaries, impurity phases etc) in doped magnesium silicide. Numerous XRD investigations of Mg_2Si-Mg_2Sn samples have shown decomposition into few $Mg_2Si_xSn_{x-1}$ solid solution phases. Redistribution of different solid solutions within the system, segregation of tin and silicon, diffusion of dopants within the system should be understood for further advancement of thermoelectric materials.

2. Results

Fourteen samples were analysed within this experiment, at room temperature, upon heating to 450°C or 600°C, some of them were previously annealed and quenched. In most cases, the thermal cycling was identical to that performed previously during synchrotron diffraction experiments. Contrasted images were successfully obtained with a pixel size of 0.547 µm. Over 10 TB of data were gathered and reconstructed into

3D images. The evolution of the microstructure of magnesium silicide based materials during thermal cycling has investigated.

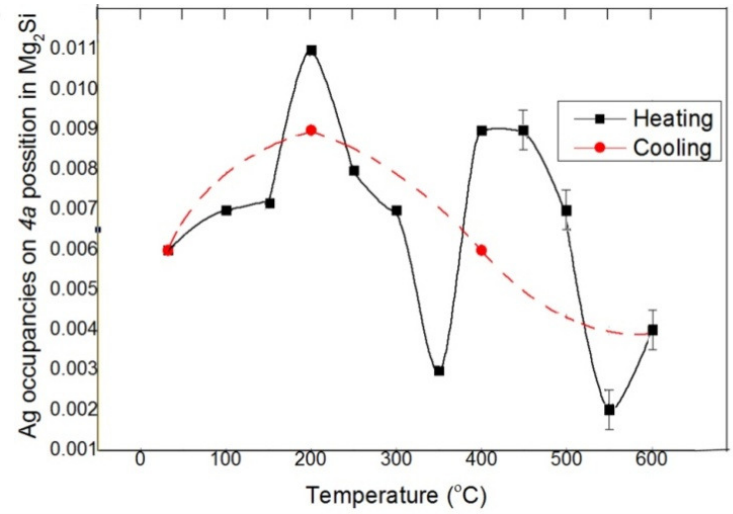

Figure 1: Change of the Ag occupancies on the Si site for the sample with nominal composition $Mg_2Si_{0.985}Ag_{0.015}$ as a function of temperature.

The first sticking result of this study concerns the stability of microstructures and the scale of phase decompositions. Unlike diffraction experiments, no dramatic changes were observed during cycling. This interesting result that cannot be clearly demonstrated by conventional microscopy analysis after sample quenching, indicates that structural transformations occur at the sub-micron scale. A detailed analysis will therefore be performed to track down any change in the voxel intensity during cycling. This requires the development of a program (ImageJ java plugin) to accurately align volumes and compensate movements induced by thermal expansion. It should allow us to potentially localise the sites where most of the change occur.

Beside the investigation of microstructure evolution, this experiment has provided precious information on microstructural features of the thermoelectric materials investigated. It revealed the various morphologies of phases obtained by the addition of different doping agents and by the use of various synthesis techniques. The figure 2 shows cases where an homogeneous solute solution is obtained and only the porosity is visible (a); few particles of intermetallic phases are observed (c) and where multiple phases and well dispersed phase are observed (b), (d) and (e).

The structure of $Mg_2Si_{0.5}Sn_{0.5}$ doped with 2% Ag synthesised by a solid state process shows a significantly different morphology from the one made by self-propagation high temperature synthesis. In the latter case, the 3D shape of the observed phases and their connectivity should allow us to shed lights of the link between TE efficiency and microstructural property. In this alloy, penetration of the dopants into the lattice doesn't change thermoelectric type of the compound, which is, however, the case of silver doping of Mg_2Si (Figure 1 (d) and (e) where the material turns from *n*-type to *p*-type. The migration of the dopants in and out of the lattice is influenced by the spatial distribution of the pure silver phase. This flux of dopants does not create significant change in the microstructure at the observed scale, however, the information obtained on the 3D

structure of the silver phase network should allow us to better understand the importance of phase distribution in manufacturing functional *p*-type. Slight variation of the amount of dopants can influence this phase distribution and the TE properties. The tomography analysis of the Mg_2Si TE material doped with 1.5% and 2.0% of Ag revealed how a variation of 0.5% of dopants can lead to some change in phase structure from small well dispersed phase Ag phase to a more connected network with more Ag-free aeras.
The silver phase acts as dopants source and sinks during cycling and therefore there spatial distribution is critical for the dynamic dopants supply. Further testing and modelling will allow us to determine which configuration is the most advantageous in the objective of tailoring phase composition and synthesis technique.

3. Conclusions

The experiment allowed us to demonstrate that migration of dopants during the thermal cycling of some Mg_2Si-based thermoelectric materials lead to microstructure change operating at the sub-micron scale.
The great variation of the structures observed between the investigated materials in particular the spatial distribution of the dopants should allowed us to gain insight into the relation between microstructure, thermoelectric type and efficiency.

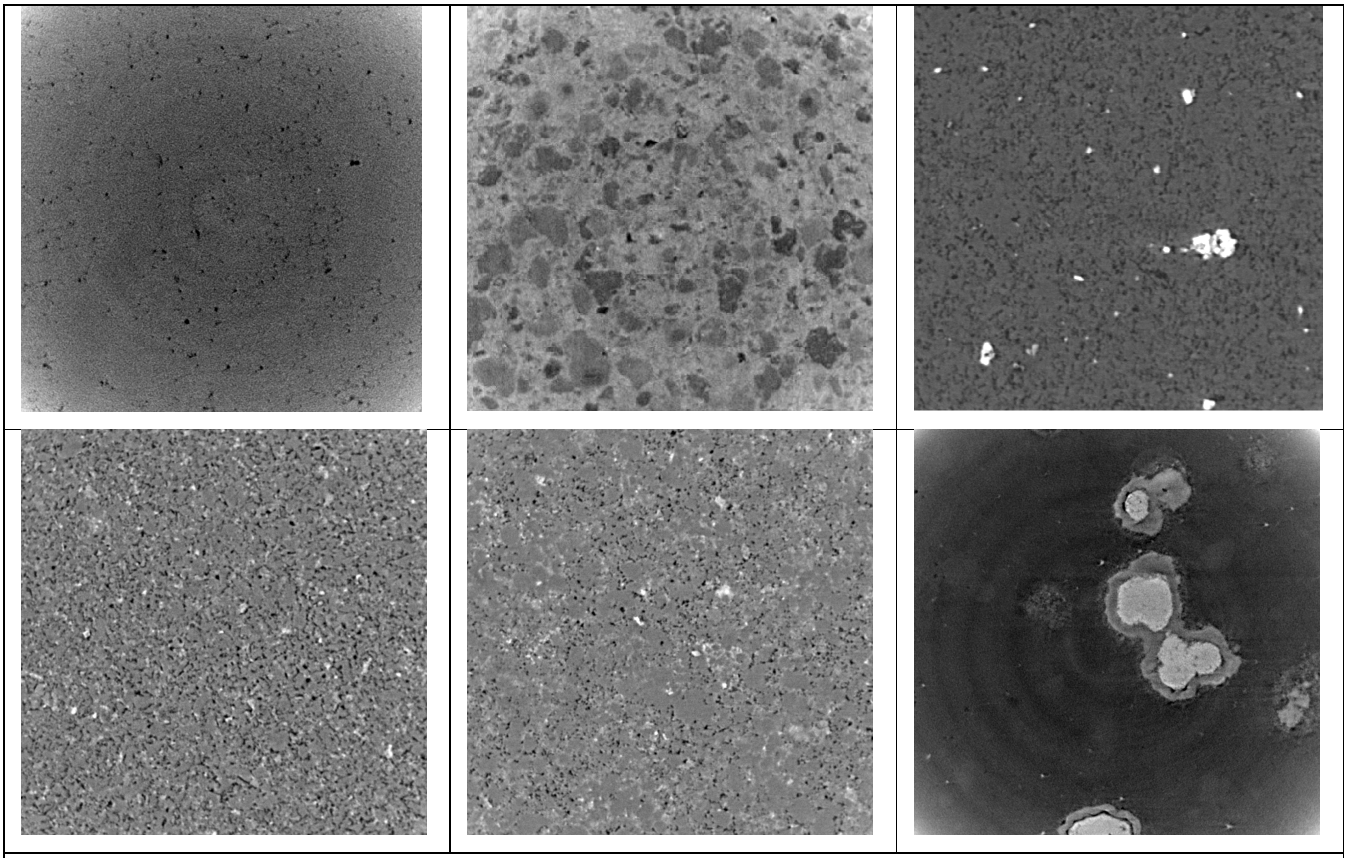

Figure 2: Extracted slices from reconstructed volumes of (a) and (b) $Mg_2Si_{0.5}Sn_{0.5}$; (c) Mg_2Si+2%Mo; (d) Mg_2Si+1.5%Ag; (e) Mg_2Si+2.0%Ag and (f) $Mg_2Si_{0.6}Ge_{0.4}$+2%Bi with Ni diffusing from thermoelectric n-type coating. (Picture size : $(550\ \mu m)^2$). The TE materials (a), (c) and (f) were synthesised by a solid state process while (b), (d) and (e) by a self-propagation high temperature synthesis.