ESRF	**Experiment title:** Nano-structured energy-harvesting thermoelectrics based on Mg2Si(1-x)Mx	**Experiment number**: MA-1690
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Shifts:	**Local contact(s)**: Yves Watier (ID31)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Malard Benoît (CIRIMAT), Anastassia Prytuliak(ESA), David Berthebaud (ENSICAEN)

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 experiments at ESRF was to determine the importance of doping versus microstructure versus temperature when compared to the evolution of the TE properties. One of the perspective routes to increase figure of merit of thermoelectric materials is a doping and co-doping with small quantities of additional elements to alter band structures, as well as purposely shifting the peak figure of merit temperature by changing doping concentrations. To understand the nature of the doping influence on the properties it is important to understand the doping distribution in Mg_2Si lattice, besides that investigation of high temperature phase transformations, including the doping atoms behavior is of high importance.

2. Results

Twelve samples were measured during the experiment, five of them with the in-situ heating up to 600 °C and cooling. For the high temperature experiments the capillaries with the powder samples were prepared under the He atmosphere, heating up the samples was provided by hot air blower.

Analysis of Mg_2(Si-Sn) samples with small amounts of Sb doping have show the presence of multiple solid solution phases with different silicon-tin ratios (Fig.1). Despite nominal composition of the samples declares 0.4/0.6 silicon-tin ratio, it was established that the main phase (~70%) has it as 0.3/0.7 respectively. Whereas the samples with a high amount of tin in the composition have shown the highest thermoelectric properties a problem of their phase stability arise after the analysis. The samples of almost the same composition produced recently contained 4 solid solution phases, the same time those which were produced a while before had already 6 solid solution phases.

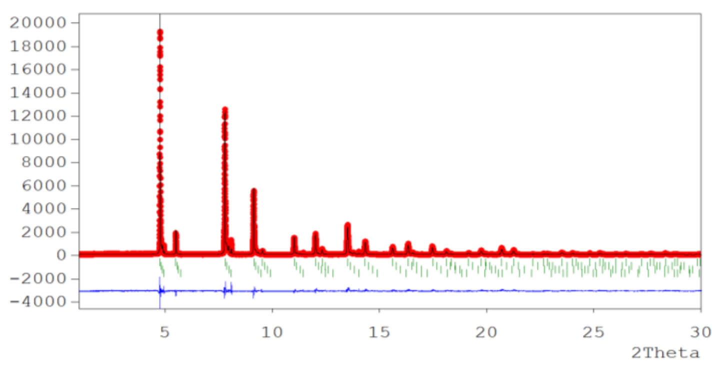

Figure 1: Typical diffraction pattern recorded from $Mg_2(Si_xSn_{1-x})_ySb_{1-y}$ samples

One of the most important results for the understanding of the doping-properties influence nature was obtained from the silver doped samples. The in-situ analysis was provided up to 600°C with the subsequent cooling. The diffractogram pattern from the Ag-doped sample at the room temperature is presented on the Fig.2 a. As can be seen from the Fig.3 the change of Ag occupancies with the temperature correlates with Seebeck coefficient change. Also it was observed that after 300 °C minor amount of Ag appears in the sample, the same time not identified phase (Ag containing phase?) at 5.59° disappear (Fig. 2b,c). Change of Ag occupancies with the temperature in samples produced in the different laboratories and using different methods have the same character and the same accordance to the properties change. For the samples doped with Bi no change of doping occupancies was observed, character of the temperature dependence of thermo power for the bismuth doped samples does not differ from the pure Mg_2Si.

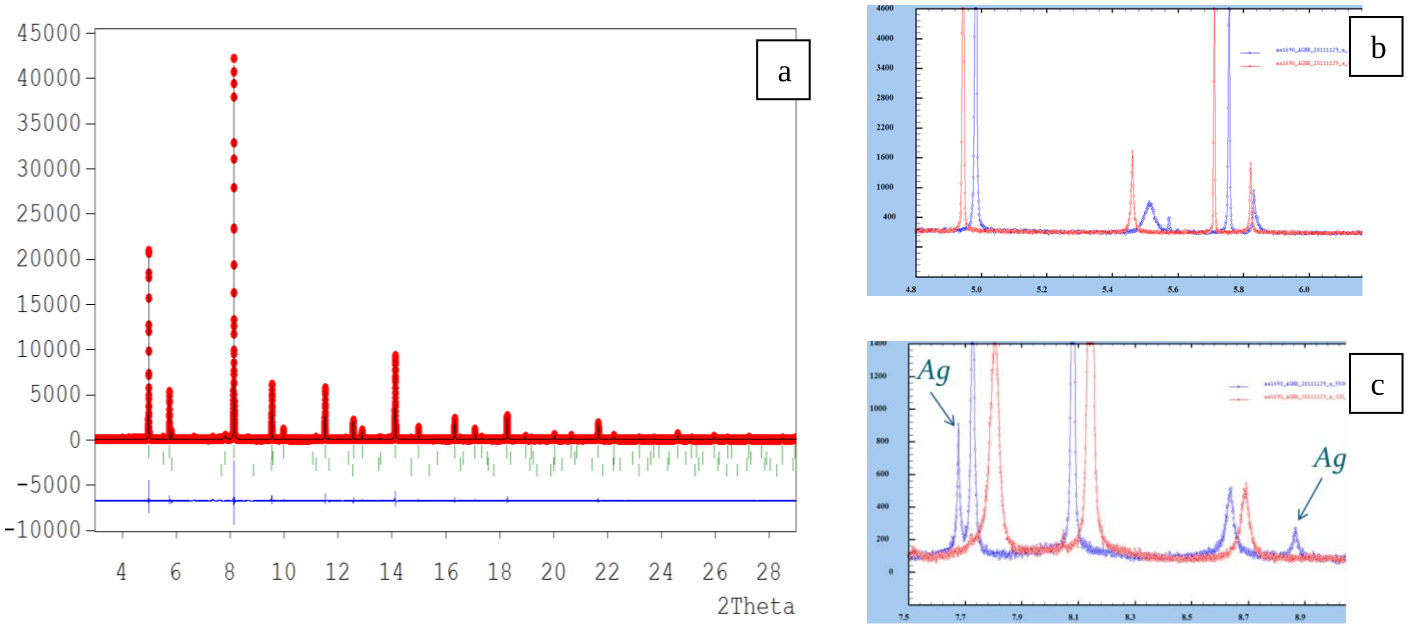

Figure 2: a – Diffraction pattern recorded from Ag doped Mg_2Si sample; b – Fragments of the diffraction patterns recorded from Ag doped Mg_2Si sample at 32°C (blue) and 550°C (red), indicating the minor change in the phase composition; c – Fragments of the diffraction patterns recorded from Ag doped Mg_2Si sample at 32°C (red) and 550° C(blue), indicating the appearance of a pure Ag phase at the high temperature.

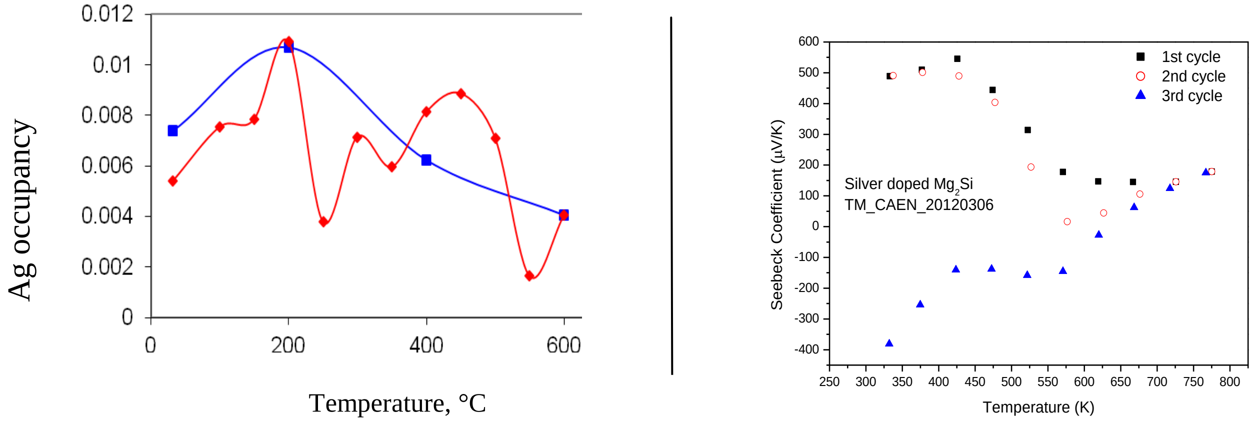

Figure 3: a – Temperature dependence of silver occupancies on the silicon in Mg_2Si doped samples, red curve - heating, blue curve -cooling; b – temperature dependence of Seebeck coefficient for Mg_2Si samples doped with Ag.

3. Conclusions

The experiment allowed us to establish a link between the dopants content in the lattice and the thermoelectric properties. Besides this, obtained information about phase compositions and phase compositions changes with the time and temperature was important for the future decision about which of the compositions and dopants are perspective for future investigation and which are not.