Experimental report

12/01/2022

Proposal: CRG-2769 **Council:** 4/2020

Title: Crystal structure(s) in nanograined Fe2Val polycrystals for thermoelectric applications

Research area:

This proposal is a new proposal

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Experimental team:

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Samples: Fe2V1.03Al0.97

Instrument	Requested days	Allocated days	From	To
D1B	1	1	09/09/2020	10/09/2020

Abstract:

Report on experiment "**Crystal structure(s) in nanograined Fe_2VAl polycrystals for thermoelectric applications", N° 2769, 9/9/2020.**

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Bi_2Te_3 is currently the reference material for thermoelectric applications at 300 K since it is commercialized in thermoelectric modules. The Heusler alloy Fe_2VAl could be considered as a substitute to Bi_2Te_3. Its chemical elements are indeed non-toxic and inexpensive, and it favourably displays a large Seebeck coefficient and a large electrical conductivity. However, its thermal conductivity is large and leads to a dimensionless figure of merit 10 times smaller than in Bi_2Te_3, hence unsuitable for applications. To solve this problem, we reduced the grain size of Fe_2VAl by grinding this material in a high energy ball-mill, followed by a fast-sintering process (Spark Plasma Sintering) to make densified bulk polycrystals with grain size ~ 1 µm. As grain boundaries are barriers to heat transport, increasing their number helps decrease the thermal conductivity.

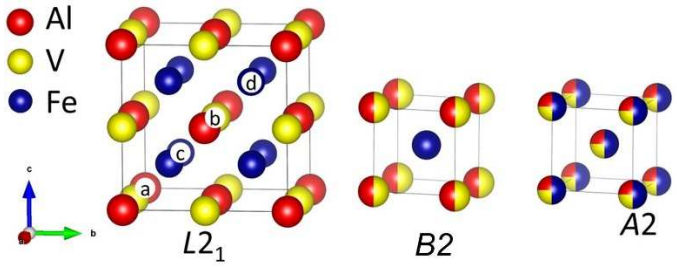

Fig. 1. Depending on thermo-mechanical history, Fe_2VAl shows 3 structures: fully ordered $L2_1$ at 25°C, partially disordered B2 above 1080°C and fully disordered A2 above 1190°C.

Fe_2VAl crystallizes at room temperature in the fully ordered $L2_1$ structure and transforms at 1080 °C and at 1190 °C into partially disordered B2 and fully disordered A2 variants respectively (Fig. 1). In the B2 structure, the Al and V atoms are mixed on the same crystallographic site whereas the Fe atoms remain on their site. In the A2 structure, all the atoms are mixed on the same site. From powder X-ray diffraction (XRD), we have shown that Fe_2VAl is very prone to cold work upon manual grinding: at 25°C under mechanical stress, the $L2_1$ structure can transform into the B2 or even the A2 structure. Given the sensitivity of Fe_2VAl to cold work, powder X-ray diffraction is unable to accurately determine how its crystal structure is disordered. Neutron diffraction is currently the best tool to achieve this goal.

Upon high energy ball milling, Fe_2VAl indeed crystallizes at 25 °C in the metastable A2 structure. Upon Spark Plasma Sintering at 900 °C, the $L2_1$ structure is at least partially restored. We thus measured on D1B a ball milled sample as a function of temperature up to 900°C, to understand in-situ how the annealing process restores the $L2_1$ crystal structure.

The in-situ experiment on the ball milled sample was carried out in the ILL high-temperature furnace (25 – 1600 °C). The diffractometer and the furnace were controlled remotely through the Nomad interface. A 1 K / min ramp was programmed. Unfortunately, the furnace did not ramp up at the programmed rate, but it heated up uncontrollably at 600 °C in few minutes. At this temperature, the $L2_1$ structure was already restored and the A2 -> B2 and B2 -> $L2_1$ transitions were missed.

The sample was anyway further annealed at 900°C and cooled down in the high temperature ILL furnace. The Rietveld refinement of the ball milled sample, which has been in situ annealed at 900°C is shown in Fig. 2. The occurrence in the pattern of the 111 and 200 lines is characteristic of the $L2_1$ structure. We could obtain a good fit by considering excess Fe on the V and Al sites and no further

disorder. These extra Fe atoms arise from a contamination of the sample by the steel balls used for milling. This shift from stoichiometry was confirmed by Electron Probe Micro Analysis. The actual Fe composition found from the neutron data is $Fe_{2.36}V_{0.77}Al_{0.87}$. The parameters of the fit are gathered in the following table. It can be concluded that the $L2_1$ structure is fully restored after sintering at 900°C.

Atom	Coordinates	B_{iso}	Occupancy
V	(0,0,0)	0.55	0.77
Fe	(0,0,0)	0.55	0.23
Al	(1/2,1/2,1/2)	0.55	0.87
Fe	(1/2,1/2,1/2)	0.55	0.13
Fe	(1/4,1/4,1/4)	0.55	2
$\chi^2 = 1.39$, $R_{wp} = 9.8\%$, $R_B = 3.25\%$			

Fig. 2. Rietveld fit of the ball-milled sample after in-situ annealing at 900°C