Experimental report

07/09/2022

Proposal:	**CRG-2553**	**Council:**	4/2018
Title:	In situ investigation of nitrogenation process of (ND,Ce)Fe10CoTialloys		
Research area:			

This proposal is a new proposal

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Samples: (Nd,Ce)Fe10CoTi

Instrument	Requested days	Allocated days	From	To
D1B	4	2	23/09/2018	25/09/2018

Abstract:

Experimental Report– Proposal CRG-2553 (D1B) – 23-24/09/18

“In-situ investigation of nitrogenation process of (Nd,Ce)Fe_{10}CoTi alloys”

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The global market has been experiencing an uprise on the consumption of rare earth elements, in particular, for permanent magnets (PM) applications. Tetragonal $R(Fe,M)_{12}$ compounds (R=rare earth, M transition), with the $ThMn_{12}$ structure, are good candidates as permanent magnet materials with reduced R content [1]. However, some thermal and structural stability issues have to be overcome. Typical structural stabilizing elements (M=Ti, V, Mo…) prefer to occupy the 8i site in the structure, which corresponds to the largest Fe moment for the $ThMn_{12}$ structure. Unfortunately, this leads to a decrease in saturation magnetization. On the other hand, in order to have applicability as permanent magnets, these compounds need to have uniaxial magnetocrystalline anisotropy; however, Nd compounds show planar anisotropy. This drawback can be overcome by nitrogenation, which is also known to enhance the Curie temperature and the anisotropy field of $ThMn_{12}$-type alloys [2].

A recent study on the intrinsic magnetic properties of $CeFe_{11-y}Co_yTi$ [3] has revealed that Co at $y\approx1$ retains the favorable uniaxial magnetocrystalline anisotropy H_a (~1.7T) found in the parent $CeFe_{11}Ti$ alloy, while enhancing the Curie temperature T_C (~312ºC) and saturation magnetization $4\pi M_S$ (12.1 kG). These findings warrant further optimization around Co substitution y=1 to try to exploit the hard magnetic properties of these Ce-based magnets. The anisotropy field of the samples might increase up to 4-fold after nitrogenation [4].

In this sense, we produced samples with 3 different stoichiometries of the series $Nd_{1-x}Ce_xFe_{10}CoTi$ (x=0, 0.5 and 1) by arc melting. Thermal treatments were subsequently carried out in order to homogenize the compounds. In order to compensate the rare-earth loss during the synthesis and promote the formation of the desired 1:12 phase, 10% excess of R was added [5,6]. Afterwards, these ingots were ground into powders. Half of the sample was sieved in order to select only those grains smaller than 40μm. Thus, we brought 6 samples to D1B but 3 compositions. The structure and purity of the samples were studied by means of X-ray diffraction (XRD). The results indicate that all samples consist of the 1:12 phase after homogenization. Magnetization measurements were carried out in a VSM with μ_0H up to 1.8T, confirming the anisotropy field μ_0H_a ~ 1.7T of the $CeFe_{11}CoTi$ alloy.

A vanadium sample holder was fabricated in ILL in order to measure the samples. These samples were embedded into quartz ampoules, in N_2 atmosphere. Firstly to avoid oxidation and secondly to perform the nitrogenation studies. Thus, the only nitrogen that the samples might have absorbed is that inside the ampoule. The nitrogenation process is expected to happen at 450ºC, as it was obtained in our lab. Thus, we measured the neutron diffraction of our samples for several hours at a steady temperature.

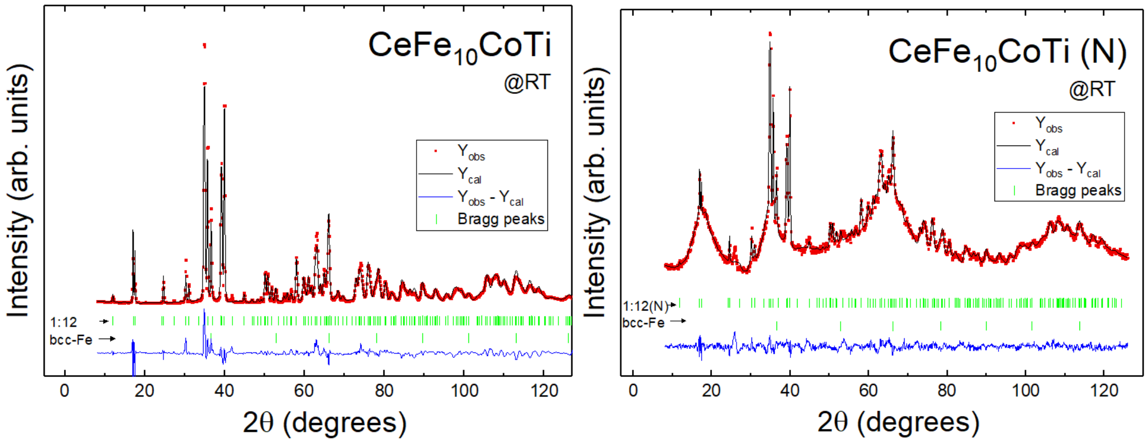

Figure 1. Rietveld refinements of the ND patterns for the $CeFe_{10}CoTi$ sample before (left) and after (right) nitrogenation. Patterns were collected at room temeperature, so nuclear + magnetic contributions are observed. Rietveld refinement only takes nuclear contributions into account.

As an example, in Figure 1 we are showing the Rietveld refinement of the sample CeFe$_{10}$CoTi, before and after nitrogenation. It is complicated to observe clear differences between the two patterns, as in the nitride sample there exist a large background. Although these are preliminary analyses, the Rietveld refinement was performed including nitrogen in the interstitials and we could see an improvement than if nitrogen was not taken into account.

Moreover, we want to extract the magnetic structure from the ND patterns substracting the nuclear contribution (at 450ºC, above T$_C$) from the nuclear+magnetic signal (at RT, below T$_C$). Although we have not done these analyses yet, we can see in Figure 2 that there exist subtle differences between the two patterns (at high and low T). For example, we can see, in the inset of Fig.2, that the intensities ratio of the Bragg peaks change when we go above T$_C$.

However, much more precise analyses must be done to obtain the magnetic structure of these alloys.

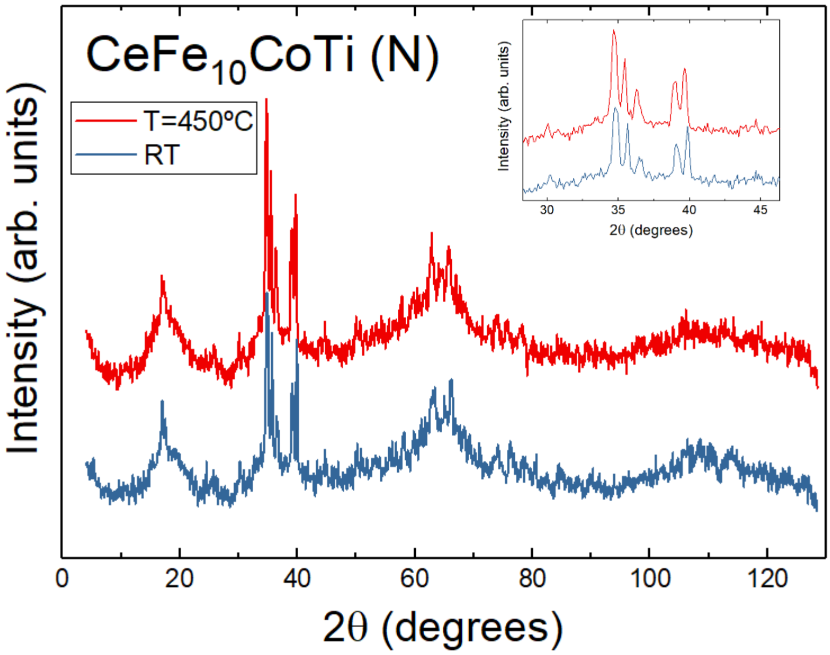

Figure 2. ND patterns of the CeFe$_{10}$CoTi alloy after nitrogenation, measured at RT (blue) and 450ºC (red).

On the other hand, as in experiment CRG-2554 we had a problem with the sample and it was not possible to measure it (because of the sample), we decided to measure these samples at very low T to see if there was a spin reorientation (as it has been observed in other 1:12 alloys) where the anisotropy change from uniaxial to planar. We had time only to measure one sample: the CeFe$_{10}$CoTi alloy. However, no spin reorientation was observed in the 1.5-300K temperature range.

References:

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