Experiment Report Form

ESRF	**Experiment title:** *In situ* XAS investigation of a novel sintering method for fabricating rare-earth-free permanent magnets	**Experiment number**: MA-5460
Beamline: BM23	**Date of experiment**: from: 14/02/2023 to: 20/02/2023	**Date of report**: 30/09/2023 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: J.E.F.S. Rodrigues (support from A. Rosa)	

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Report:

Our research group has recently developed and patented a novel cold sintering method for manufacturing $SrFe_{12}O_{19}$-based magnets that allows obtaining dense pieces (≈92%) with magnetic properties comparable to medium-high grade commercial ferrites,[1] while at the same time decreasing the energy consumption in 9 kWh/kg (energy savings >30% compared to the sintering methods employed industrially).[1], [2] In brief, the method involves the following steps: (i) mixing the magnetic powders ($SrFe_{12}O_{19}$) with an organic solvent, (ii) applying simultaneous pressure and temperature (190 °C), and (iii) annealing the sample at higher temperature (1100 °C).

The present beamtime experiment was intended to replicate this sintering protocol inside a diamond anvil cell (DAC) coupled to an appropriate heater system, with the aim of monitoring the structural changes occurring to $SrFe_{12}O_{19}$ upon simultaneous application of pressure and temperature. For this purpose, we collected time-resolved X-ray absorption spectroscopy (XAS) data at BM23-ESRF at two different energies: Sr *K*-edge (16.105 keV) and Fe *K*-edge (7.112 keV) and powder X-ray diffraction (PXRD), using a beam size of 3x3 μm^2. For the described experiment, we used various pairs of 300 and 600 µm NPDs (full and perforated NPDs for Sr and Fe *K*-edges, respectively) from BM23/ID24 stock. The DAC loading was different for each edge: while solid loading (and uniaxial pressure) was used for Sr *K*-edge runs, a thin pellet was immersed in silicone oil (pressure medium) for Fe *K*-edge runs, with which the applied pressure was isostatic in this case. Different heating systems were employed for each edge as well.

Figure 1(left) shows XAS and PXRD data collected at the Sr *K*-edge during sintering of magnetic $SrFe_{12}O_{19}$ powders (SFO) following the routine: (i) initially, the sample is subject to a small pressure (1.0 GPa), (ii) then, heated up to 190 °C and (iii) maintained at that temperature for 2 hours, (iv) to finally continue to increase the temperature up to 400 °C. Pressure was measured during each sintering step based on diffraction data on Au, mixed with the sample, although unfortunately, this was not possible for the last part. The first derivatives of the XANES spectra (not shown here) unveil edge displacement towards lower E values, indicating a mild reduction of the Sr^{2+} cations through the sintering process. As the experiment advances, the whiteline loses intensity and the oscillations are attenuated, suggesting amorphization of the sample. Small changes are also observed on the FT of the EXAFS spectra, in particular, a shift of the Sr-O distance, while no significant changes are observed on the PXRD data.

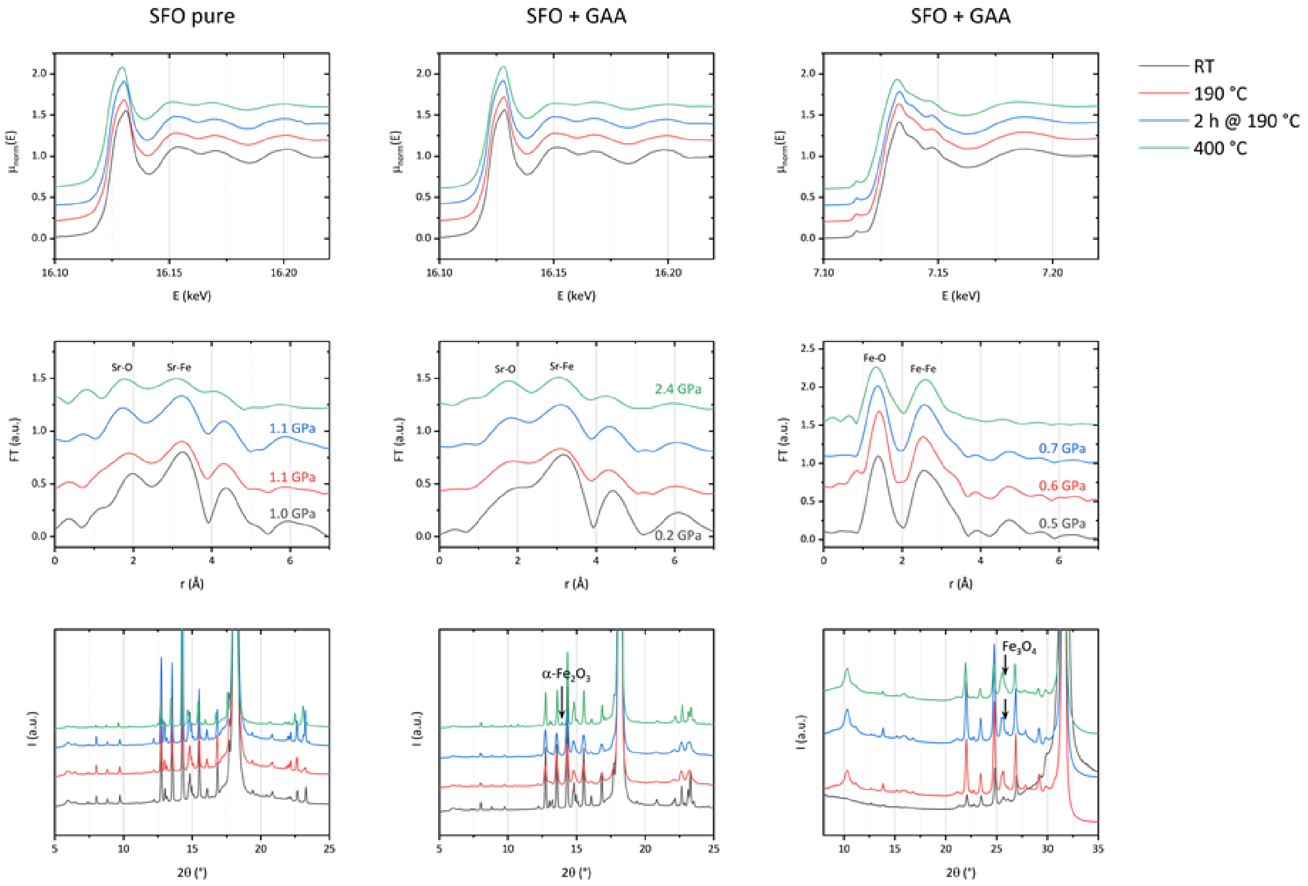

Figure 1. (left) XANES spectra at the Sr K-edge, Fourier transform modulus of EXAFS at the same edge and PXRD patterns collected during sintering pure $SrFe_{12}O_{19}$ (SFO). (center) The same for SFO mixed with glacial acetic acid (GAA). (right) XANES spectra at the Fe K-edge, Fourier transform modulus of EXAFS at the same edge and PXRD patterns corresponding to sintering SFO + GAA.

The data shown in Figure 1 (center) was collected during a second sintering experiment in which the same sintering route was followed except that in this case, SFO was mixed with an organic solvent (glacial acetic acid, GAA). In this case, the oxidation state of the absorbing atom (i.e., Sr) in the starting material (SFO+GAA) is even lower than the last stage of the previous experiment, and the Sr reduction further advances as the experiment continues. In this case, PXRD reveal a small amount of α-Fe_2O_3. Based on previous studies,[1] amorphous SrO could be forming as well, although simulations of the XAS spectra is required to get confirmation. This second experiment was intended identical to the first one (except for GAA addition). However, the built up pressure during heating was higher in this case (2.4 GPA) so unfortunately, the experiment was not fully comparable to the twin experiment without GAA. Therefore, it is not possible to conclude whether α-Fe_2O_3 forms as a consequence of the added solvent or of the higher pressure.

The same experiment was carried out, now measuring at the Fe *K*-edge (see Figure 1(right)), although unfortunately, the observations are not really compatible. In this case, XANES suggests reduction of Fe^{3+} while formation of a small amount of Fe_3O_4 after heating for 2 hours at 190 °C is visible from PXRD. Although the two last experiments were intended to resemble identical sintering processes, different iron oxides were formed. Unfortunately, it is difficult to state whether this is simply a consequence of the different DAC assembly used for both edges (described above). We suspect the silicone oil used to mount the sample to measure at the Fe *K*-edge (great amount compared to the GAA added to the sample) might definitely have an influence on the pH, which must be changing the chemistry of the system completely.

During this experiment, good quality data was collected. However, the chemistry of the system changed compeltely when minutirizing the experiment to load samples in a DAC, yielding different behaviour compared to what we expected from our previous experience. We well continue exploring the data and carrying out further experiments to achieve better understanding of the processes and phase changes undergone. Once we understand better, we will build a complete and publishible story well-supported by these data.

[1] A. Serrano *et al.*, “Hexaferrite-based permanent magnets with upper magnetic properties by cold sintering process via a non-aqueous solvent,” *Acta Materialia*, vol. 219, p. 117262, Oct. 2021, doi: 10.1016/j.actamat.2021.117262.

[2] A. Serrano, E. García, J. F. Fernández, C. Granados-Miralles, and A. Quesada, “Procedimiento de obtención de un imán permanente de cerámica magnéticamente anisótropo y denso,” WO 2021/160909 A1, 2021