ESRF	**Experiment title:** **Time-resolved XRD studies of combustion synthesis reactions in applied magnetic fields**	**Experiment number**: HS-1588
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Report:

High-resolution time-resolved X-ray diffraction (TRXRD) experiments were performed on ID11. Data were recorded at a rate of one pattern every 135 ms, comprising 60 ms exposure time and 75 ms readout time from a 1024 × 1024 pixel FRELON CCD camera. Excellent counting statistics were obtained, enabling Rietveld analysis, as illustrated in Fig.1.

Two different self-propagating high-temperature synthesis (SHS) reactions were tested:

1. $BaO_2 + 6\ Fe + 3\ Fe_2O_3 + 4\ O_2 \rightarrow BaFe_{12}O_{19}$,
2. $MgO + ZnO + Fe_2O_3 + 2\ Fe + 0.75\ NaClO_4 \rightarrow MgZnFe_4O_8 + 0.75\ NaCl$.

Over the course of the experiment a total of 40 reactions were successfully set up and run. An initial series of 6 runs was devoted to optimising the experimental set-up, which was new in that we were using pelletised samples for the first time. Thereafter, we were able to focus on one of the main aims of the experiment – to test the repeatability of the SHS reactions – by recording 16 runs each of reactions 1 and 2, half of which were performed in zero field, and half of which were performed in an applied field of 0.2 T. Inspection showed that the runs were indeed repeatable.

The runs were also qualitatively analysed to determine the effect of the 0.2 T applied field on the combustion wave. In the case of $MgZnFe_4O_8$, reactions in zero field were found to take ca. 1.0 s, whereas in 0.2 T the reaction times were ca. 0.6 s – clear evidence, in keeping with other observations, that the applied field leads to faster combustion rates.

Quantitative Rietveld analysis of the reactions (Fig. 1) has been very informative. One completely new result, revealed from our fits to the reaction 2 pre-ignition scans, was that some combustion already takes place during the mixing, grinding and pellet pressing step. It is likely that this is due to the volatility of the sodium perchlorate reactant in the mixture. This result sheds some light on previous work where a noted difficulty was that ostensibly identical pre-SHS mixtures had significantly different ignition characteristics. We plan to follow this up with a study of controlled mixing, grinding and pressing procedures.

Some difficulties were encountered in the Rietveld analysis. In fitting the intermediate and post-combustion reaction 2 scans we were hampered by a lack of previously established data on the cationic distribution of the $Mg_{0.5}Zn_{0.5}Fe_2O_4$ end product. Even such basic information as the expected lattice parameter and the spinel inversion parameter are not known. Thus, although our fitting has been largely satisfactory it is not entirely clear which results are specific to the combustion route.

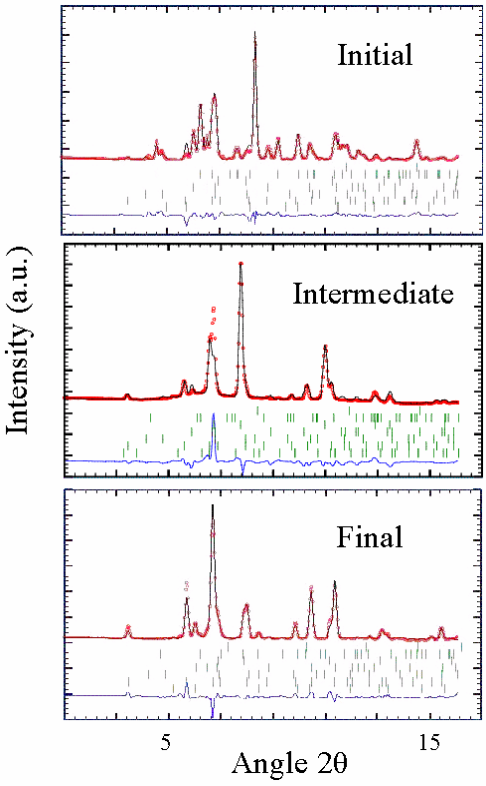

Fig. 1. Rietveld fits of TRXRD data from the combustion synthesis reaction of MgO, ZnO, Fe, Fe_2O_3 and $NaClO_4$ to form the magnesium ferrite product $Mg_{0.5}Zn_{0.5}Fe_2O_4$.

The Rietveld analysis also revealed some problems with the 0.2 T data, where the conversion from two-dimensional to one-dimensional scans resulted in unexpected line broadening, not apparent in the two-dimensional patterns. This is though to be most likely due to stray field from the 0.2 T Sm-Co magnets affecting the X-ray detector.

Towards the end of the experiment we attempted some pellet reactions in high-field (1.1 T) magnet. This proved to be particularly difficult, with the thin pellet samples being prone to disintegration in the large field gradients. Nevertheless, two successful runs were obtained.