Experimental report

02/09/2026

Proposal: DIR-238 **Council:** 4/2021

Title: Charge and magnetic order in novellayered double perovskites LnBaFe2O6 (Ln = Nd, Y) containing unusually high mixed valence Fe3.5+

Research area: Materials

This proposal is a new proposal

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Samples: LnBaFe2O6 (Ln = Nd,Y)

Instrument	Requested days	Allocated days	From	To
D2B	2	2	02/07/2021	05/07/2021

Abstract:

This research forms part of a jointly funded EPSRC and JSPS UK-Japan collaborative project. We have used low-temperature topotactic ozone oxidation for A-site layer ordered oxygen deficient LnBaFe2O5 and obtained fully-oxidized double perovskites LnBaFe2O6. The compounds contain unusually high mixed valence Fe3.5+ ions, and are thus expected to show charge transitions to relieve the electronic instability of Fe3.5+. Temperature dependent magnetic susceptibility revealed complicated and successive transitions, e.g. a ferromagnetic-like sharp increase at 320 K, followed by a decrease at about 260 K for NdBaFe2O6. In the proposed NPD experiments, we want to clarify the complicated charge disproportionation/ordering and magnetic transition behaviours of LnBaFe2O6. 2 days on D2B are needed to study 1g Ln = Nd and Y samples over a range of temperatures.

Charge and magnetic order in novel layered double perovskites *Ln*$BaFe_2O_6$ (Ln = Nd, Tb) containing unusually high mixed valence $Fe^{3.5+}$

Mixed valence states of transition-metal ions in oxides often cause intriguing physical properties. A famous example is the Verwey transition in magnetite Fe_3O_4 [1,2]. Another recent interesting example is seen in A-site-layer-ordered oxygen-deficient double perovskite $LnBaFe_2O_5$ (Ln: lanthanoids), in which the mixed valence $Fe^{2.5+}$ state causes a Verwey-type charge ordering accompanying large changes in magnetization and unit cell volume [3]. We have explored novel materials containing unusually high and mixed valence transition-metal ions and investigated the charge transition behaviours.

We have used low-temperature topotactic ozone oxidation for A-site layer ordered oxygen deficient $LnBaFe_2O_5$ and obtained fully oxidised double perovskites $LnBaFe_2O_6$. The compounds contain unusually high mixed valence $Fe^{3.5+}$ ions, and are thus expected to show charge transitions to relieve the electronic instability of $Fe^{3.5+}$.

In this experiment, around 800 mg of Ln = Nd and Tb were measure at D2B using V-foil can and wavelength of 1.594 Å. For Ln = Nd, scans were collected at 340, 300, 260, 150 and 1.5 K with each counting 4 hour. For Ln = Tb, scans were collected at 400, 300, 100 and 5 K with each counting 4 hours. Neutron diffraction shows long range magnetic ordering together with a structural transition at first transition, indicating a charge disproportionation. The neutron diffraction patterns in Figure 1 clearly show the magnetic signal below first transitions, as well as relative magnetic intensities changes upon cooling. $TbBaFe_2O_6$ show an extra Tb ordering at 5 K with pronounced magnetic reflections. Further analysis will be carried out to understand these spins structures and investigate potentially spin reorientations.

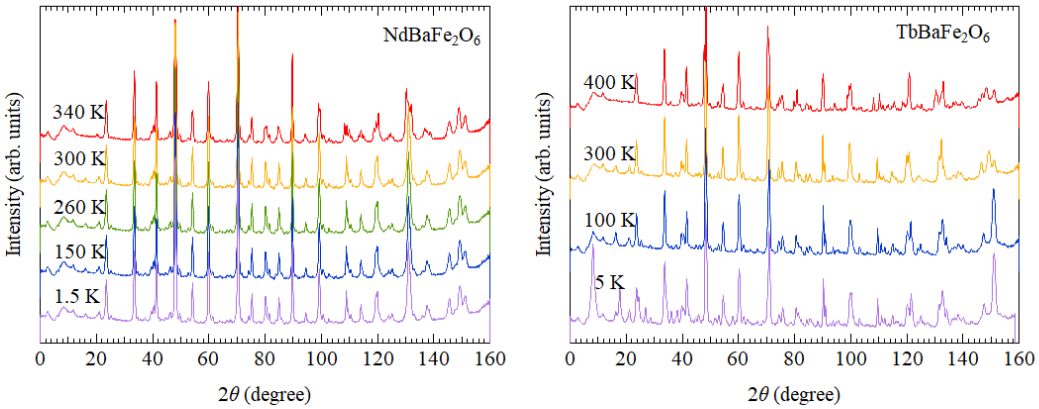

Fig. 1 Temperature dependent neutron diffraction patterns for Ln = Nd and Tb.

References

1. E.J.W. Verwey, Nature 144, 327 (1939).
2. M. Senn. J.P. Wright, J.P. Attfield, Nature 481, 173 (2012).
3. P. Karen, J. Solid State Chem. 177, 281 (2004).