Experimental report

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Council: 10/2014

Title: Investigation of Nuclear and Magnetic Structures in A-site Ordered Spinel LiFeCr4O8

Research area: Materials

This proposal is a new proposal

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Samples: LiFeCr4O8

Instrument	Requested days	Allocated days	From	To
D2B	1	2	28/04/2015	30/04/2015
D20	1	0		

Abstract:

We have been investigating the dielectric and magnetic properties of A-site ordered spinel, LiFeCr4O8 in view of multiferroic properties. The parent compound LiGaCr4O8 shows a strong magnetic frustration and undergoes antiferromagnetic ordering at very low temperature (14 K), while the compound with Fe3+ ion at the A-site shows multiple magnetic transitions; first it undergoes a ferrimagnetic ordering at high temperature (100 K) followed by two magnetic transitions at around 50 K and at 24 K and the latter is coupled with a structural transition. Interestingly, we observe ferroelectric polarization below 24 K suggesting that this compound is a magnetoelectric multiferroic. In order to understand the role of magnetic structure on the electric properties and magneto-structural coupling in LiFeCr4O8, we need to carry out a detailed investigation of the magnetic and nuclear structure of this material at different temperatures.

Investigation of Nuclear and Magnetic Structures in A-site Ordered Spinel $LiFeCr_4O_8$

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Powder sample of $LiFeCr_4O_8$ prepared by conventional solid state route was used to perform the neutron diffraction experiment. The diffraction experiment was carried out on the D2B diffractometer at the Institut Laue-Langevin (ILL) using ~ 2.5 g sample packed in a vanadium can of diameter 6.2 mm. The experiment was performed using two different wavelengths of 1.59 and 2.4 Å. For the treatment of diffraction data FULLPROF suite program was used [1].

From the Rietveld analysis of room temperature neutron data we observe that the compound crystallizes in the cubic structure with the space group $F\bar{4}3m$ as shown in Fig. 1(a). From the the analysis of temperature dependent neutron data we observe that the compound remains in the cubic structure down to 25 K. Based on the Rietveld refinement performed on the 3.5 K data we find that the diffraction pattern fits well with the tetragonal structure with the space group $I\bar{4}m2$ as shown in Fig. 1(c). To model this two nuclear structures we have used powder pattern collected with $\lambda = 1.59$Å. In Fig. 1(d) and (e) we show the schematics of cubic (298 K) and tetragonal (3.5 K) nuclear structures respectively obtained from the refinement.

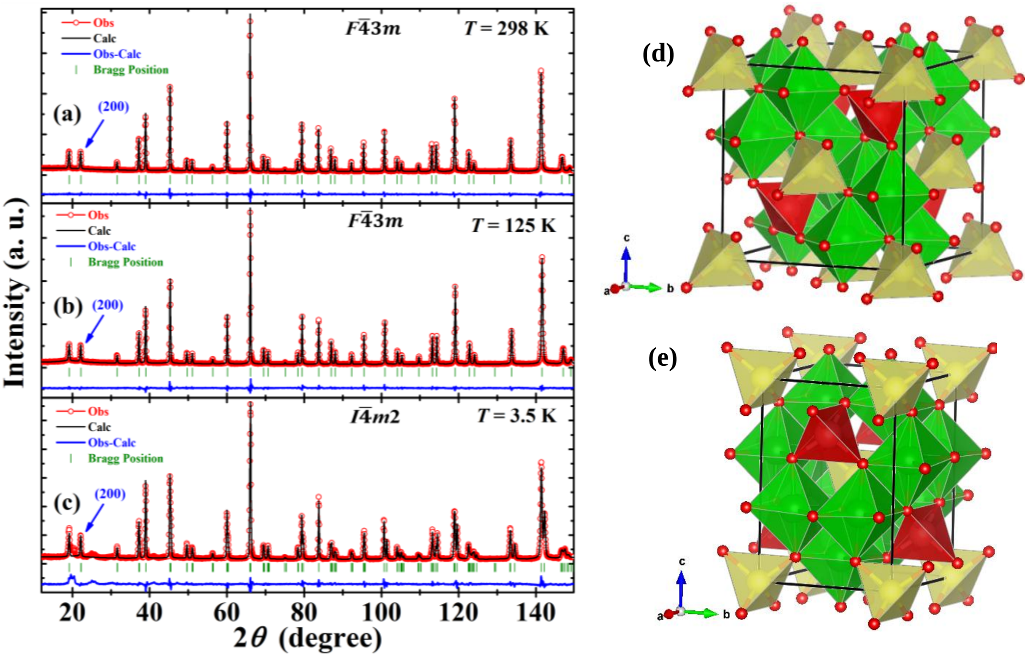

FIG. 1. (a-c) Rietveld refinements on the neutron diffraction pattern of $LiFeCr_4O_8$ collected at T = 298, 125 and 15 K with λ = 1.59 Å; Schematic representation of (d) cubic ($F\bar{4}3m$) and (e) tetragonal ($I\bar{4}m2$) structure of $LiFeCr_4O_8$ obtained from the Reitveld refinement on neutron diffraction pattern collected at 298 and 3.5 K using a wavelength of λ = 1.59 Å. The polyhedra with yellow, red and green contain the Li, Fe and Cr atoms respectively. (Unindexed peak at 3.5 K corresponds to the magnetic contribution)

In the cubic structure Li^+ and Fe^{3+} ions occupy the 4*a* and 4*d* Wyckoff sites, Cr^{3+} and two O^{2-} ions occupy the 16*e* crystallographic sites respectively, while in the tetragonal phase Li^+ and Fe^{3+} ions occupy the 2*a* and 2*d* Wyckoff sites and Cr^{3+} and two O^{2-} ions occupy the 8*i* crystallographic sites as observed in the tetragonal structure of MgV_2O_4 [2]. Neutron diffraction patterns recorded at all temperatures contain the (200) reflection which is a signature of ordering between Li^+ and Fe^{3+} ions located at the *A*-site.

To investigate the magnetic structures associated with the crystallographic structures we have performed Rietveld analysis on the neutron powder pattern collected with $\lambda = 2.4$ Å as shown in Fig. 2. The magnetic structure determination has been accomplished following the representation analysis technique of group theory described by Bertaut [3,4]. Since we do not observe any new reflection other than increase in intensity on top of some nuclear reflection [Fig. 2(a)] in the temperature range $30 \leq T \leq 100$ K, the propagation vector $k = (0, 0, 0)$ was considered. We have found that the refinement of the magnetic structure by considering the representation Γ_4 gives the best fit to the observed diffraction patterns at $30 \leq T \leq 100$ K i.e., below the magnetic ordering temperature. The fitted pattern at 30 K is shown in Fig. 2 (b) and the corresponding magnetic structure is shown in Fig. 2 (d). The magnetic structure is a collinear ferrimagnetic (Fe^{3+} and C^{r3+} ions are aligned antiparallel) in nature with the ordered magnetic moment aligned along the crystallographic *c* direction with a net magnetic moment of 1.991 μ_B.

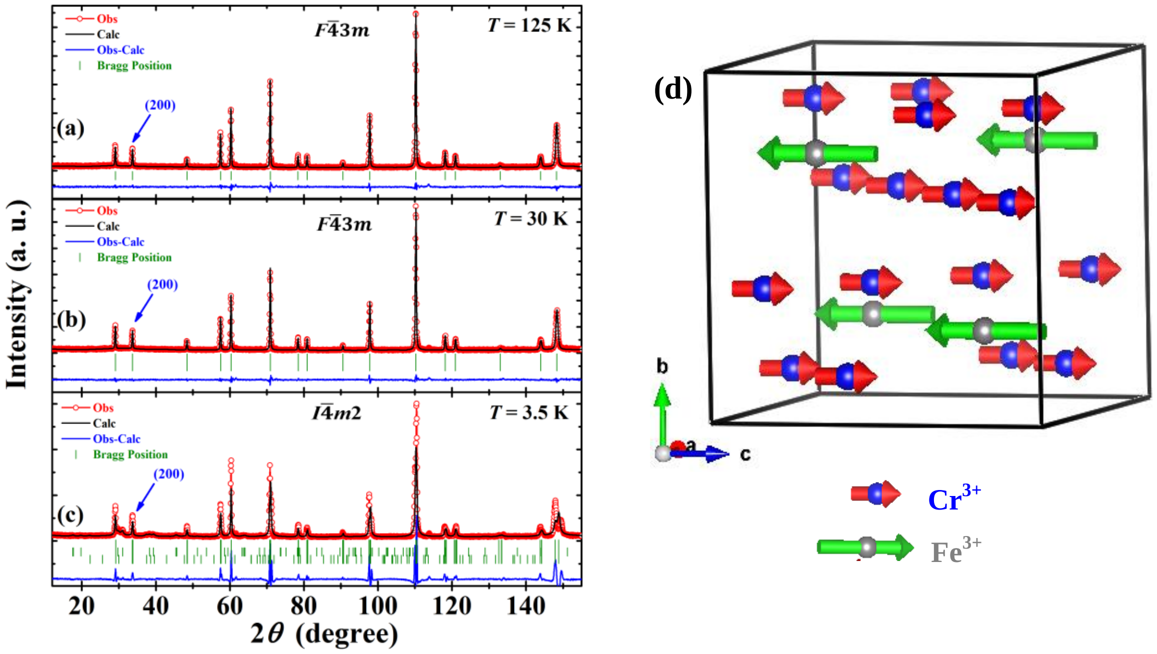

FIG. 2. (a-c) Rietveld refinements on the neutron diffraction pattern of $LiFeCr_4O_8$ collected at *T* = 125, 30 and 15 K with $\lambda = 2.4$ Å; Schematic representation of (d) ferrimagnetic structure of $LiFeCr_4O_8$ obtained from the Reitveld refinement on neutron diffraction pattern collected at 30 K. The second Bragg position in Fig. 2(b) correspond to the magnetic reflection. In Fig. 2(c) the second and third Bragg reflections correspond to the magnetic contribution associated with k_1 and k_2 propagation vectors.

From the investigation of nuclear structures of $LiFeCr_4O_8$ we have observed a structural phase transformations from cubic ($F\bar{4}3m$) to tetragonal ($I\bar{4}m2$) symmetry at around 25 K. Preliminary modelling on the neutron powder pattern collected at 3.5 K shows the presence of two different propagation vectors $\mathbf{k_1}$ = (0.4960 0.4378 0.5) and $\mathbf{k_2}$ = (0.25 0.25 0.2360) respectively indicating that the spin structure probably adopts complex noncollinear arrangement which is under investigation.

References

[1] J. Rodríguez-Carvajal, Physica B: Condens. Matter 192, 55 (1993).

[2] E. M. Wheeler, B. Lake, A. N. Islam, M. Reehuis, P. Steffens, T. Guidi, and A. H. Hill, Phys. Rev. B 82, 140406 (2010).

[3] E. F. Bertaut, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press, New York, 1963), Vol. 3.

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