

FA2-MS14B-T05

Pressure-Induced Long Range Charge Order in LuFe₂O₄. J. Rouquette^a, J. Haines^a, A. Al-Zein^a, Ph. Papet^a, J. Bourgeois^b, A. Maignan^b and Ch. Martin^b.

^aICG UMR CNRS 5253 (C2M), Place Eugène Bataillon, cc1503, 34095 Montpellier cedex 5, France.

^bLaboratoire CRISMAT, ENSICAEN, UMR 6508 CNRS, 14050 Caen Cedex, France.

E-mail: Jerome.Rouquette@univ-montp.fr

Although multiferroics are rare, the mechanisms giving rise to multiferroicity are shown to originate from particular balance between charge-spin-orbital and lattice parameters. Lutetium ferrite (LuFe₂O₄) appears as an ideal candidate to study multiferroic properties as it exhibits a frustrated structure, which is shown to be directly linked to electronically driven ferroelectricity. Additionally, upon cooling, ferrimagnetically ordered spins can be observed below 240 K giving rise to particular coupling of the sequential charge ordering and spin. Further interesting properties linked with spin - charge order coupling have recently been reported such as magnetoelectric response, giant magnetic coercivity or strong insulating behavior for this material. The crystal structure of LuFe₂O₄ consists of an alternating stacking along *c* of hexagonal Fe₂O_{2.5} bilayers and LuO_{1.5} layers. Owing to the ordered charge distribution of the Fe²⁺ and Fe³⁺ species on triangular lattice of the bilayers, each bilayer has a dipole moment and the system is ferroelectric below the charge-ordering temperature T_{CO} ≈ 320 K, which can be determined based on Mössbauer spectroscopy, neutron or electronic diffraction. The exact full three-dimensional charge configuration determining the net electric polarisation of the material is however under debate from a theoretical and experimental point of view. The supercell detected by neutron diffraction, is reported to have $\sqrt{3} \times \sqrt{3}$ charge ordered structure in the *ab* plane along the [110] direction. Single crystal X-ray scattering studies proposed an antiferroelectric ground state stacking of the charge order associated with an incommensurate propagation close to (1/3, 1/3, 3/2), while diffuse scattering at 360 K with (1/3, 1/3, 0) propagation indicated ferroelectric short-range correlations between neighboring double layers.

Here, we present a high-pressure structural study of LuFe₂O₄ by X-Ray diffraction[1]. As the electric polarization arises from the special charge order of Fe²⁺-Fe³⁺ in this material, pressure can be expected to decrease the distance between the distinct iron positions in the triangular lattice and hence increase the electronically driven ferroelectricity. Such a scenario has already been observed in manganites and shows that pressure is probably an appropriate parameter to better understand electronically-driven ferroelectricity. A very recent study was reported on the pressure effects on LuFe₂O₄ up to 2.5 GPa by ac susceptibility and electronic transport measurements showing that pressure tends to suppress the magnetic state. In this work, we will show that higher pressure induces an irreversible phase transition to a long range charge order structure with $\sqrt{3} \times \sqrt{3} \times 2$ orthogonal supercell. This arrangement can easily be explained by the distinct local compressibility of the Fe²⁺-based and Fe³⁺-based triangular oxygen bi-pyramids. Such a long range charge order structure, recoverable at atmospheric pressure, is of great interest for an electronically-driven ferroelectric material.

[1] J. Rouquette, J. Haines, C. Martin et al., PRL (submitted).

Keywords: LuFe₂O₄, Pressure, Charge Order

FA2-MS14B-T06

Crystal Chemistry of Manganese containing Perovskites related to Calcium Aluminate Cements. S. Stöber^a, G. Redhammer^c, O. Prokhnenko^b, S. Schorr^b, & H. Pöllmann^a.

^aInstitut für Geowissenschaften Mineralogie/Geochemie, Martin-Luther-Universität D-06120 Halle (Saale). ^bBENSC Hahn - Meitner Institut Berlin. ^cUniversität Salzburg Materialforschung und Physik.

E-mail: stefan.stoeber@geo.uni-halle.de

With the improvement of iron rich CAC cement properties due to intergrinding and sintering of Mn - secondary raw materials and cement raw meal, perovskite phases contain significant concentrations of Mn³⁺/Mn⁴⁺ ions, dependent on the oxygen fugacity (fO₂). Brownmillerite phases, structurally described as oxygen deficient perovskites, can compensate certain amounts of Mn⁴⁺ due to incorporation of additional oxygen, but will become unstable and dissolve into Alumina rich Iron - Manganese - Brownmillerites Ca₂(Al,Mn,Fe)O_{5+d} [3] and Perovskite Ca(Mn,Ti,Fe)O_{3-d}. Beside the typical layer sequence of tetrahedra (t) - octahedra(o) in brownmillerite type structure, different stacking sequences can be stabilised due to the variation of fO₂. These structures are built up of different sequences like oo or too. In order to investigate these phases, samples with the chemical compositions CaAl₂O₅ - CaFe₂O₅ - CaMn₂O_{5+d} and CaFeO_{3-d} - CaMnO_{3-d} - CaTiO₃ were synthesised either as powders by sol - gel methods or as single crystals. The crystal structures were refined using neutron diffraction techniques at the BENSC E6 of the Helmholtz - Centre Berlin for Materials and Energy, the manganese valences were determined by iodometric titration. The valence state of iron was determined by Mössbauer - spectroscopy. The phases with the chemical composition Ca(Fe,Mn,Ti)O_{3-d} with ABO₃ type structure crystallise predominately in space group Pnma. With the incorporation of trivalent iron the space group changed to I4/mcm and finally into Pm3m. The phase transition is also dependent on the temperature level, which was proofed by high temperature XRD

Phase with the chemical composition Ca₃(Fe,Mn,Ti)₃O_{8+d} (n = 3 A₃B₃O_{8+d}) [1], [2] were only synthesised purely in a narrow range as long as enough iron filled the tetrahedrally coordinated sites in the crystal structure..

[1] Rodriguez-Carvajal, J. Mat. Res. Bull., 24: p. 423-430. (1989)[2] Nguyen N., et al., J. Solid State Chemistry., 53: p. 398-405. (1984) [3] Redhammer G. J., et al., Am. Miner., 89: p. 405-420. (2004.)

Keywords: Perovskite, Brownmillerite, Neutron Diffraction