Experimental report

05/11/2015

Proposal: **5-31-2328** **Council:** 4/2014

Title: Crystallographic and magnetic study of a new series of polymorph $Li_2M(SO_4)_2$ for Li-ion batteries.

Research area: Chemistry

This proposal is a new proposal

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Samples: $Li_2M(SO_4)_2$ M=Fe, Co, Ni, Mn and delithiated phases

Instrument	Requested days	Allocated days	From	To
D20	4	3	01/12/2014	04/12/2014

Abstract:

We have recently discovered a new series of polymorphs of general formulae $Li_2M(SO_4)_2$ (M = Fe, Co, Mn, Ni) which present very good potentialities as Li-ion battery materials. Indeed lithium can be extracted from $Li_2Fe(SO_4)_2$ according two plateau at 3.73 and 3.85 V vs. Li^+/Li^0, which is much higher than the most praised iron-based material $LiFePO_4$ (3.45 V). The two plateaus indicate the presence of a single well-defined phase $Li_{1.5}Fe(SO_4)_2$ for which iron is in the 2.5+ state (possible charge ordering). Therefore we propose to study the nuclear and magnetic structure of these compounds with two aims: (i) determine the Li position of the pristine and delithiated materials $Li_{1.5}Fe(SO_4)_2$ and $Li_1Fe(SO_4)_2$, (ii) explore the magnetic structure of the $Li_xM(SO_4)_2$ phases as we expect it to reveal new physics (magnetoelectric properties, charge ordering effects at low T). Temperature-dependent magnetic susceptibility measurements show that a long-range magnetic order is established below about 30-50 K (depending on the sample). We ask for 4 days on D20 to measure the following compounds: $Li_2M(SO_4)_2$ (M = Fe, Co, Mn, Ni) and the two delithiated phases $Li_{1.5}Fe(SO_4)_2$ and $Li_1Fe(SO_4)_2$.

Proposal 5-31-2328 – Experimental report

Crystallographic and magnetic study of a new series of polymorph $Li_2M(SO_4)_2$ for Li-ion batteries

In the last twenty years Li-ion batteries conquered the portable electronics market and are nowadays considered as a strong contestant for electric vehicles and smart-grid energy storage systems. However, to reach for such applications, high energy density electrode materials based on low-cost, abundant and environmental benign elements are required, where the most promising material so far has been the olivine $LiFePO_4$ (3.45 V *vs.* Li^+/Li^0 and ~150 mAh/g). In the quest of finding new high energy density materials, our group focused amongst others on sulfate-based compounds. This research lead to the discovery of a peltry of new phases including the family of monoclinic *marinite* disulfates $Li_2M(SO_4)_2$ (M = 3d transition metals) prepared via a solid-state ceramic route, where especially the iron-based compound presents a particularly elevated redox potential of 3.83 V *vs.* Li^+/Li^0.[1]

Determining the magnetic structure of the monoclinic *marinite* phases $Li_2M(SO_4)_2$ (M = Fe, Co, Mn) from neutron powder diffraction, it has been shown that these compounds solely allow super-super-exchange interactions between the transition metals for the establishment of the long-range antiferromagnetic order, which can be explained by their particular structural framework of FeO_6 octahedra and SO_4 tetrahedra.[1,2] By changing the synthesis approach and applying a mechanical-milling synthesis route, we were able to stabilize $Li_2M(SO_4)_2$ phases (M = Fe, Co, Ni, Zn, Mn), which crystallize in an orthorhombic unit cell isostructural to $Li_2Ni(SO_4)_2$ (space group: *Pbca*).[3,4] Similarly to the *marinite* monoclinic compounds $Li_2M(SO_4)_2$ (M = Co, Fe, Mn), the structure of these orthorhombic phases is built on isolated MO_6 octahedra, which are interconnected through SO_4 tetrahedra (Fig. 1). The main difference between the monoclinic and orthorhombic polymorphs is nested in the way the MO_6 and SO_4 polyhedra are interconnected, and as a consequence, the M–M distances in the orthorhombic structure are shorter than the M–M ones (M = Fe, Co, Mn) in the *marinite* monoclinic structure. This prompted us to further investigate the magnetic properties of the orthorhombic polymorph.

Magnetic measurements using a SQUID magnetometer on the orthorhombic compounds $Li_2M(SO_4)_2$ (M = Fe, Co, Ni, Mn) have shown that they all order antiferromagnetically at low temperature (10 K < TN < 45 K depending on the nature and the transition metal; see Fig. 1). We therefore studied the nature of the magnetic structure of the samples $Li_2Fe(SO_4)_2$, $Li_2Co(SO_4)_2$, $Li_2Mn(SO_4)_2$, as well as the delithiated phases $Li_{1.5}Fe(SO_4)_2$ and $Li_{1.0}Fe(SO_4)_2$ using a long wavelength (2.41 Å) of D20 to obtain high quality data at low angles in order to solve the magnetic structures of these compounds. The successfully conducted experiment clearly showed the appearance of additional magnetic peaks due to the long-range ordering of the magnetic moments (Fig. 1). Furthermore, the occurrence of the magneto-electric effect in the orthorhombic compounds that has already been shown for the isostructural $Li_2Ni(SO_4)_2$ compound,[5] could have been confirmed with help of the neutron powder diffraction (NPD) experiment.

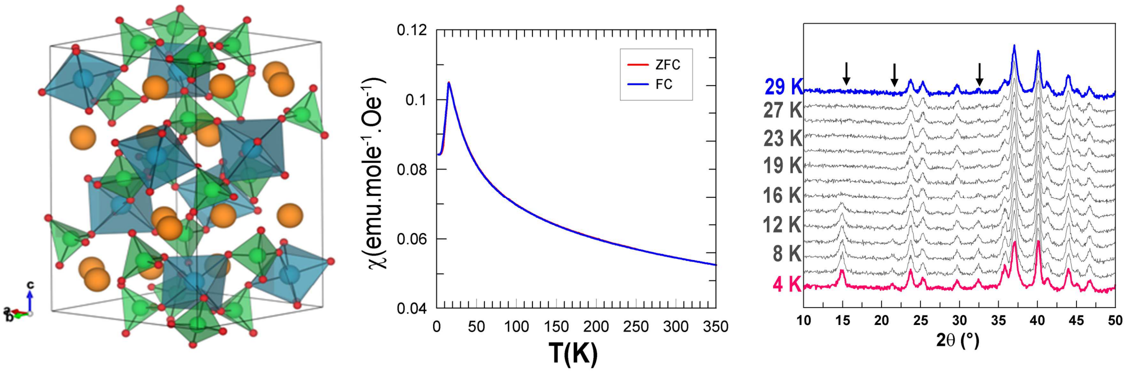

Figure 1 : From left to right: Structure of $Li_2Fe(SO_4)_2$ showing the interconnection of the blue FeO_6 octahedra through the green SO_4 tetrahedra. Orange and red balls represent the lithium and oxygen atoms, respectively. Temperature dependent magnetic susceptibility of $Li_2Co(SO_4)_2$ indicating the occurrence of a long range antiferromagnetic ordering. NPD patterns of $Li_2Co(SO_4)_2$ upon heating showing the additional magnetic peaks (black arrows).

Besides the interesting magnetic properties, we were also intrigued by the electrochemical performance of orthorhombic $Li_2Fe(SO_4)_2$ that revealed two successive biphasic processes at 3.73 V and 3.85 V vs Li^+/Li^0 (Fig. 2) with the formation of an intermediate $Li_{1.5}Fe(SO_4)_2$ before reaching the delithiated phase $Li_{1.0}Fe(SO_4)_2$. In order to get more insight into the structural features of the delithiated phases, NPD measurements using the high resolution configuration of D20 were performed with a wavelength of λ = 1.54 Å at 100 K. The results allowed us to validate our models for the phases $Li_{1.5}Fe(SO_4)_2$ and $Li_{1.0}Fe(SO_4)_2$ (refinement see Fig. 2) and particularly to accurately localize the lithium atoms in the structure, which is not precisely feasible from laboratory X-ray powder diffraction data.

In conclusion, the conducted NPD experiments on the D20 diffractometer allowed us to solve the magnetic structure of the new orthorhombic $Li_2Fe(SO_4)_2$ polymorph and get a detailed insight into the two-step delithiation mechanism upon electrochemical cycling. Two manuscripts with obtained the results are currently in preparation.

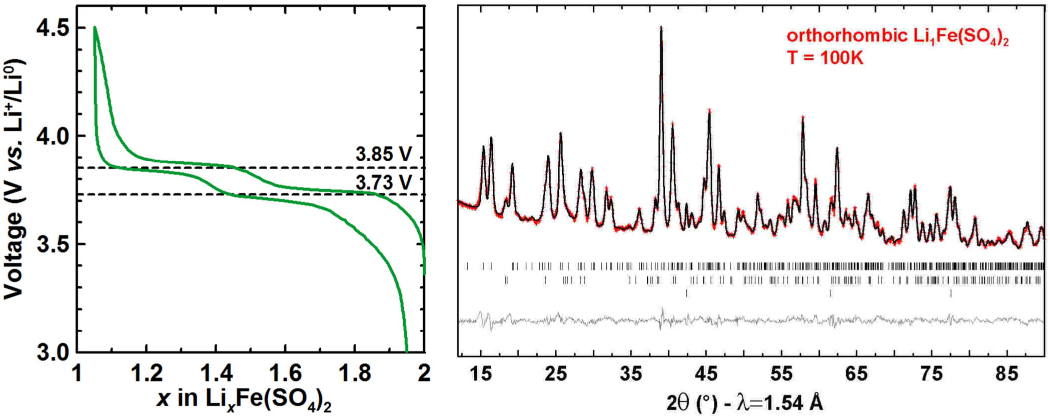

Figure 2 : From left to right: Voltage-composition trace of orthorhombic $Li_2Fe(SO_4)_2$ with the two plateaus at 3.73 V and 3.85 V vs. Li^+/Li^0. Rietveld refinement of delithiated $Li_{1.0}Fe(SO_4)_2$ recorded at 100 K (the second and third phases are $FeSO_4.H_2O$ and vanadium (sample holder) respectively).

References

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