Experimental report

26/10/2016

Proposal:	**5-21-1099**	**Council:**	4/2015
Title:	Cation order / disorder in magnesium transition metal borates. Potential electrodes for Mg-ion batteries		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:

$MgCo_2(BO_3)_2$
$Mg_2Co(BO_3)_2$
$Mg_{1.5}Co_{1.5}(BO_3)_2$
$MgMn_2(BO_3)_2$
$Mg_2Mn(BO_3)_2$
$MgNi_2(BO_3)_2$
$Mg_2Ni(BO_3)_2$
$MgMnB_2O_5$
$Mg_{2/3}Mn_{4/3}B_2O_5$

Instrument	Requested days	Allocated days	From	To
D2B	2	2	04/11/2015	06/11/2015

Abstract:

New mixed metal borates containing magnesium and a transition metal ion have been synthesized, and the materials show promise as Mg-ion battery cathodes. The polyanion framework forms layers or channels of magnesium, allowing Mg-ion diffusion. It is possible to alter the ratio of Mg/transition metal, and the choice of transition metal (Mn, Co or Ni) determines whether cation ordering occurs. From our X-ray diffraction analysis it is not possible to determine the boron and oxygen positions and we have therefore been unable to determine the affect changing the transition metal, Mg/TM ratio, and cation ordering has on the crystal structure. Neutron diffraction would allow the O and B positions to be determined, aiding our understanding of these materials, and how structure relates to performance as a Mg-ion cathode material.

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Background and motivation

Magnesium-ion batteries are a potential successor to lithium-ion technologies. They offer higher theoretical capacities due to the use of a divalent working ion, and Mg metal can be used as the anode, providing a benefit in terms of both cost (Mg is abundant) and safety (dendrite formation and thermal runaway are not thought to be an issue, unlike in Li-ion).

Magnesium transition metal borates, of which there are a large number of potential structures, are of interest as cathode materials due to:

- Their open frameworks which may facilitate Mg-ion transport
- Lightweight polyanion group which increase voltages through the inductive effect and allows for high specific capacities
- Wide variety of structures and oxidation states allowing manipulation of capacity and redox chemistry.

We have synthesized $MgMnB_2O_5$ and $Mg_{2/3}Mn_{4/3}B_2O_5$ which both show promise as cathode materials for Mg-ion batteries, with up to half the Mg being reversibly removable from the structure.

X-ray diffraction of the layered borates ($MgCo_2(BO_3)_2$, $Mg_2Co(BO_3)_2$ and $Mg_{1.5}Co_{1.5}(BO_3)_2$) show significant cation ordering, with Co sitting almost exclusively on site 1, the more symmetric octahedra. Ni and Mn versions show less cation ordering however as X-rays are not sensitive to B and O positions the effect on the borate framework is unknown.

Experimental aims

Neutron diffraction collected on D2B at room temperature was used to study the pyroborates are various states of charge to assess structural changes during Mg-ion cycling. As the cathodes are nanoparticles full structural analysis was unlikely, but changes in cell parameters and appearance of new reflections aid understanding of the mechanism.

The effect of varying the transitions metal and transition metal to magnesium ratio in the layered borates was also studied with the aim of understanding changes in the borate framework and cation ordering.

Results

Pyroborates at various states of charge

Table 1 shows refined data (combined powder neutron and powder x-ray) for the pristine pyroborate structures compared to literature values for the end members, and show synthesis of a solid solution.

Table 1: Refined cell parameters for the solid solution (MgMn)$_2$B$_2$O$_5$

$Mg_xMn_{2-x}B_2O_5$	$X = 0$[1]	$X = \frac{2}{3}$	$X = 1$	$X = \frac{4}{3}$	$X = 2$[1,2]
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
χ^2		2.15	3.33	11.7	
R_{wp}		20.1	19.7	9.88	
Vol (Å^3)	189.53	185.172(9)	181.365(1)	179.131(6)	171.48/171.33
M1 occ (Mn/Mg)	1/0	0.73/0.28(1)	0.647/0.353(8)	0.403/0.597(6)	0/1
M2 occ (Mn/Mg)	1/0	0.61/0.39(1)	0.353/0.647(8)	0.264/0.736(6)	0/1
Average M1-O (Å)		2.196(10)	2.173(5)	2.131(7)	
Average M2-O (Å)		2.160(10)	2.142(5)	2.139(7)	

Analysis of data collected for the pyroborates (Figure 1) at various states of charge shows significant volume changes consistent with Mg removal from the structure and Li insertion. On removal of Mg there is a 4.2% reduction in volume. It is worth noting that although there are few crystalline peaks, it appears that the polyanion framework is retained even after removing 50% of the cations. Subsequent Li insertion increases the volume by just 1%. This is a small volume change for a relatively high capacity of Li cycling. This is accompanied by a doubling of the unit cell in the *c* axis, suggesting cation ordering of some sort.

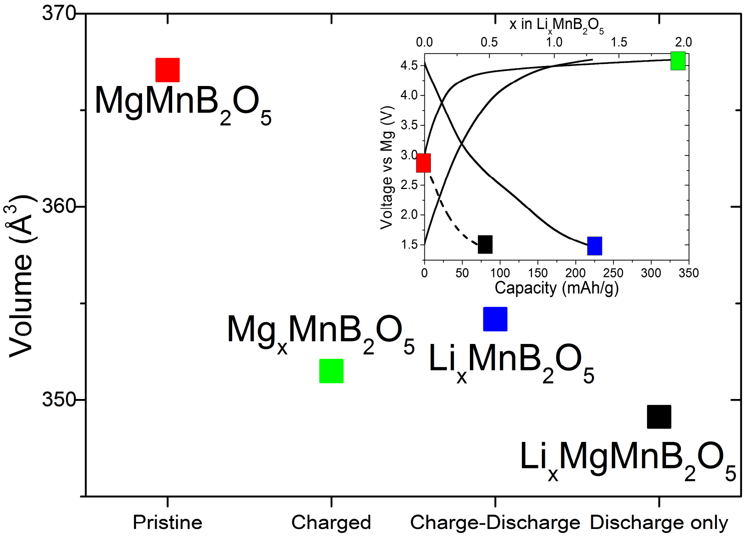

Figure 1: Unit cell volumes for x=1 pyroborate at various states of charge.

Layered borates

Structures obtained from refinement of ILL data show cation ordering in the Co and Ni version, and lack of order in the Mn version, consistent with powder X-ray diffraction. The added sensitivity to B and O have allowed complete structure refinements for the series of compounds and show that all 3 transition metals, at all metal to magnesium ratios, crystallise in the Pnmn space group. There is also a linear change in cell parameters, with increasing cell volume with increasing transition metal content, suggesting formation of a solid solution. Figure 2 shows a representative refinement.

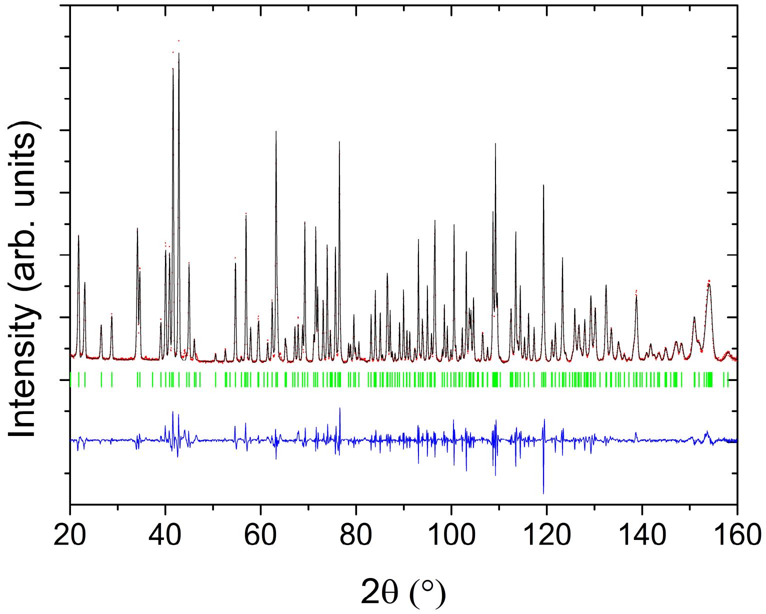

Figure 2: Refinement of ILL collected powder neutron data from a combined x-ray and neutron refinement for $Mg_2Co(BO_3)_2$.

Conclusions

Data collected on D2b at ILL helped allowed determination of cell volume changes during cycling of a new Mg-ion and Li-ion cathode – $MgMnB_2O_5$. Sensitivity to boron and oxygen not observed in lab X-ray data allowed full structural refinements for a series of layered borates.

Both these studies will be included in my PhD thesis and are being prepared for publication.

References

1. Block, S., Burley, G., Perloff, a. & Mason, R. D. Refinement of the crystal structure of triclinic magnesium pyroborate. *J. Res. Natl. Bur. Stand. (1934).* **62,** 95 (1959).

2. Guo, G. C., Cheng, W. D., Chen, J. T., Huang, J. S. & Zhang, Q. E. Triclinic Mg2B2O5. *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **51,** 351–353 (1995).