Defect-tolerant diffusion channels for Mg^{2+} ions in ribbon-type borates: structural insights into potential battery cathodes MgVBO_4 and $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$

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ABSTRACT: The reversible room temperature intercalation of Mg^{2+} ions is difficult to achieve, but may offer substantial advantages in the design of next-generation batteries if this electrochemical process can be successfully realized. Two types of quadruple ribbon-type transition metal borates ($\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ and MgVBO_4) with high theoretical capacities (186 mAh/g and 360 mAh/g) have been synthesized and structurally characterized through the combined Rietveld refinement of synchrotron and time-of-flight neutron diffraction data. Neither MgVBO_4 nor $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ can be chemically oxidized at room temperature, though Mg can be dynamically removed from the latter phase at elevated temperatures (approximately 200 - 500 °C). It is found that Mg diffusion in the $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ structure is more facile for the inner two octahedral sites than for the two outer octahedral sites in the ribbons, a result supported by both the refined site occupancies after Mg removal and by bond valence sum difference map calculations of diffusion paths in the pristine material. Mg diffusion in this pyroborate $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ framework is also found to be tolerant to the presence of Mg/Fe disorder since Mg ions can diffuse through interstitial channels which bypass Fe-containing sites.

INTRODUCTION

While Li-ion battery technologies are currently dominant for mobile electronics applications, the growing demand for inexpensive and safe energy storage options for large-scale applications such as electric vehicles and grid scale storage has motivated recent efforts to use multivalent ions such as Mg^{2+} in rechargeable batteries¹⁻⁵. Mg-ion batteries are expected to have advantages in safety and cost, benefits primarily derived from the usage of Mg metal anodes⁶. There are still many challenges which must be overcome before Mg-ion systems are suitable for practical applications, including the challenges of designing good electrolytes, the exceedingly limited mobility of Mg^{2+} ions in most solid state frameworks, and the lack of cathodes with the high specific capacities needed to achieve sufficiently high energy densities to displace existing technologies for monovalent mobile ions⁷. It is particularly important to discover new Mg-ion cathode materials, since the very few examples of existing Mg-ion cathodes which have been robustly demonstrated to achieve substantial specific capacities⁷⁻⁸ have not led to the development of structural families which can be generally tuned to optimize battery performances, in analogy to important Li-ion battery classes such as $\alpha\text{-NaFeO}_2$ -type LiCoO_2 , spinel-type LiMn_2O_4 , or olivine-type LiFePO_4 ⁹⁻¹¹.

Borate based polyanion compounds are promising systems in which to search for novel cathodes for battery applications, since (1) their oxoanion groups provide an inductive effect that enhances the operating voltage and overall energy density relative to pure oxide analogues, and (2) among the common oxoanion groups (*e.g.*, phosphates, silicates, sulfates), the mass/charge (m/z) ratio of the borate group is the lightest, thus favoring high specific capacities. There have been a number of recent studies demonstrating the potential of borate-based compounds as high-capacity cathode materials for lithium-ion batteries¹²⁻¹³. These studies have motivated the present

investigation of magnesium metal borates for their potential utility as cathode materials in Mg-ion battery applications.

There are a number of borate structures where known examples of redox-active transition metals coexist with divalent Mg cations. For the present study, two very similar “ribbon” frameworks which contain 4 parallel chains of edge sharing octahedra (Figure 1) were studied. The orthoborate compound MgVBO_4 belongs to the warwickite structural family, which has a general stoichiometry of $M_2\text{BO}_4$ ($M = \text{Mg, Sc, Ti and Fe}$)¹⁴⁻¹⁵. In this orthoborate structure, the quadruple ribbons are connected by isolated BO_3^{3-} polyanion groups. Most known warwickite compounds have two or more cations distributed over the M sites. The one compound in this family which has a single type of M cation is Fe_2BO_4 , in which there are two very different types of Fe sites. The compound Fe_2BO_4 has superstructure peaks associated with an unusually strong charge ordering that drives nearly complete separation into sites with valences of either Fe^{2+} or Fe^{3+} below room temperature, has an incommensurate structure at intermediate temperature, and loses all evidence of charge order in the average structure at elevated temperatures when electrons become more mobile¹⁶⁻¹⁷. A second such borate framework is the $M_2\text{B}_2\text{O}_5$ pyroborate family, where the quadruple ribbons are stitched together by dimeric $\text{B}_2\text{O}_5^{4-}$ polyanion blocks. The compounds $\text{Mg}_2\text{B}_2\text{O}_5$ and $\text{Fe}_2\text{B}_2\text{O}_5$ both have the same geometric connectivity. $\text{Mg}_2\text{B}_2\text{O}_5$ can be synthesized in both a triclinic (suarite type, space group $P\bar{1}$, #2)¹⁸⁻¹⁹ and in an unnamed monoclinic polymorph (space group $P2_1/c$, #14)²⁰, while $\text{Fe}_2\text{B}_2\text{O}_5$ has only been observed in the triclinic structural type²¹. The monoclinic structure has twice the volume of the triclinic cell, a change resulting from the doubling of the b -axis of the triclinic cell.

Figure 1. Crystal structures of the M_2BO_4 (left, space group $Pnma$) and $M_2B_2O_5$ (right, space group $P\bar{1}$) family of compounds, where M denotes a divalent cation. Dashed rectangles indicate the quadruple ribbons of edge-sharing octahedra in which Mg^{2+} cations can reside. These ribbons have two distinct crystallographic sites, with the outer sites denoted as M_A (blue octahedra) and the inner sites as M_B (brown octahedra). The B^{3+} cations are found at the center of isolated BO_3^{3-} groups in the $MgMBO_4$ orthoborates and in dimeric $B_2O_5^{4-}$ groups in the $MgMB_2O_5$ pyroborates.

In both the orthoborate and pyroborate structures, there are two different crystallographic sites for the M cations, indicating two distinct environments for these cations. This has two important implications. First, when two different M cations are used in the structure, there is a possibility of partial or complete ordering over these two distinct sites. Second, the local environment is quite different for both sites and it is therefore expected that the mobility of a given ion may strongly depend on the specific site in which it is found. The outer two chains of terminal octahedra in the ribbons are both associated with one crystallographic site, denoted M_A , while the

central two chains of octahedra in each ribbon are associated with a second site, denoted M_B . In the pyroborate $M_2B_2O_5$ compounds, the quadruple-chain ribbons are isolated from each other and are arranged parallel to each other with no shared oxygens. In contrast, the ribbons in the orthoborate M_2BO_4 compounds occur in a nearly perpendicular arrangement, with each terminal M_AO_6 octahedron corner-sharing an oxygen with three central M_BO_6 octahedra in a neighboring ribbon. This triply shared oxygen site is the only oxygen site which is not part of a BO_3 triangle, and presumably its larger number of neighboring octahedra (four in total) relative to the other oxygen sites is required to satisfy the bonding and valence requirements of this shared site in the absence of bonding to borate groups.

Based on a structural analysis, it is expected that these compounds may be useful for battery applications. It is known that edge-sharing chains of MO_6 octahedra can give rise to metallic conduction, and the chains in these compounds may facilitate sufficient electronic conductivity for electrochemical cycling to be possible²². The ability of these borate frameworks to support ionic conduction is as-yet unknown and it is a goal of the present work to obtain a better understanding of potential ionic diffusion processes in these frameworks. While the focus here is on Mg^{2+} ions, it is also expected that Li^+ ions can be hosted by these structural frameworks. The ability of the ribbon frameworks to support electronic and ionic conduction will certainly depend on the structural distribution of cations over the inequivalent M_A and M_B sites at the edges and centers of the chains, and it is important to quantify the relative proportion of mobile and redox-active cations over these two types of sites. The present work investigates the structures of $MgVBO_4$, and the $Mg_xFe_{2-x}B_2O_5$ solid solution and their potential for use in Mg-ion batteries, as these two compounds both contain Mg^{2+} as a potentially mobile ion together with and V^{3+} or Fe^{2+} as the redox-active ion which can be oxidized during Mg removal.

Based on general crystal chemical principles, the presence of disorder at M_A and M_B sites is expected to be most likely when cations are similar in both valence and size. It is therefore expected that Mg^{2+} (0.72 Å) is more likely to be disordered when mixed with Fe^{2+} (0.78 Å) than with V^{3+} (0.64 Å). Disorder has been previously observed for structural analogues of both $MgVBO_4$ ($MgTiBO_4$, $MgScBO_4$) and $Mg_xFe_{2-x}B_2O_5$ ($Mg_xMn_{2-x}B_2O_5$)²³⁻²³. While the orthorhombic lattice parameters of the orthoborate $MgVBO_4$ have previously been determined for samples prepared either through conventional solid state synthesis²⁴ or by electrolysis²⁵, there have been no prior structural studies of the atomic site positions and occupancies for this compound. The triclinic pyroborates $Mg_2B_2O_5$ and $Fe_2B_2O_5$ have been previously synthesized and characterized, including both X-ray powder diffraction and single crystal diffraction studies^{19, 21, 26-27}. However, the battery-relevant solid solution compositions of $Mg_xFe_{2-x}B_2O_5$ have not previously been prepared, although closely related $Mg_xMn_{2-x}B_2O_5$ compounds have been synthesized before²³.

Bond valence sum (BVS) difference maps were utilized in this work to provide insights into the potential Mg^{2+} diffusion paths and the associated diffusion barriers in $MgVBO_4$ and $Mg_xFe_{2-x}B_2O_5$ compounds. The soft BVS parameterization for Mg^{2+} was used²⁸, rather than the classical hard BVS approach²⁹⁻³⁰, as it has been previous shown that this longer-range parameterization is more suitable for the generation of 3D maps³¹⁻³³. The BVS difference map approach calculates the valence of the target ion (*e.g.*, Mg^{2+}) at each point in a user-defined three dimensional grid according to a set of empirically parameterized bond valence parameters. From this data, plots of the absolute value of the difference $|\Delta V|$ between the ideal and calculated valence can be made in order to investigate the positions within a structure that the potentially mobile ion might be able to thermally access. In this approach, the valence is calculated from the

distance between the cation and nearby anion sites, with the valence contribution from each bond (in valence units, v.u.) increases exponentially with decreasing cation-anion distance. This method has been successfully applied to a broad spectrum of battery materials to provide specific insights into likely ion diffusion pathways and coarse estimates of their activation barriers. The size of the threshold value of $|\Delta V|$ that is needed to establish a percolation pathway provides a criterion for judging whether the barrier for diffusion is expected to be small, modest, or large. While the BVS difference map method has been commonly applied to study Li-ion diffusion, it has not previously been applied to Mg-ion systems.

In this work, polycrystalline samples of MgVBO_4 (theoretical capacity of 360 mAh/g) and $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ (theoretical capacity of 186 mAh/g based on a $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, and 295 mAh/g based on a $\text{Fe}^{4+}/\text{Fe}^{2+}$ redox couple) were synthesized and characterized through the combined Rietveld refinement of synchrotron X-ray and time-of-flight neutron diffraction. This has enabled the preliminary assessment of potential Mg^{2+} diffusion pathways through the calculation of bond valence sum difference maps. These maps were analyzed in comparison with those obtained for a few known battery compounds (FePO_4 , MgMnSiO_4 and Mo_6S_8). The removal of Mg^{2+} from MgVBO_4 and $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ has been attempted both by room temperature chemical methods and by high temperature solid state methods, enabling synchrotron X-ray and neutron powder diffraction studies of the structure of demagnesiates ribbon compounds. Based on these results, some general conclusions can be made about the factors influencing the mobility of Mg^{2+} ions within these frameworks.

EXPERIMENTAL

MgV¹¹BO₄ powders (typically ~6 g batches) were prepared using starting materials of magnesium acetate tetrahydrate (MgAc₂·4H₂O, Spectrum, A. C. S. reagent), V₂O₅ (Alfa Aesar, 99.6 % min) and ¹¹B₂O₃ (ISOTEC, 99 atom % ¹¹B). Since structural characterization by neutron diffraction was a goal, samples were prepared using ¹¹B instead of natural boron (¹⁰B is an extremely strong neutron absorber). These starting materials were mixed with a molar ratio of 2 : 1 : 1.1 in order to avoid boron deficiencies in the final product. This ratio was initially optimized for the synthesis of Mg₂¹¹B₂O₅ under similar reaction conditions, and the need for excess boron is likely associated with water absorption resulting from the strongly hydrophilic nature of B₂O₃ and/or boron volatility during the high-temperature synthesis. The precursor powders were ball milled in a zirconia ball mill jar for 100 minutes with a SPEX SamplePrep8000 Mixer/Mill high energy ball mill. The resulting powder was placed into a graphite crucible and loaded into a tube furnace which was purged with a 5% H₂/95% N₂ mixture (“forming gas”) for approximately 30 minutes. The sample was then reacted at 1200 °C for 10 hours under flowing forming gas (~30 mL/min). Enriched Mg_xFe_{2-x}¹¹B₂O₅ ($x = 2/3$ and $4/3$) samples were synthesized in an equivalent manner using MgAc₂·4H₂O (Spectrum, ACS grade reagent), FeC₂O₄·2H₂O (Alfa Aesar, 99%) and ¹¹B₂O₃ (ISOTEC, 99 atom % ¹¹B) as starting materials, but with a lower final reaction temperature of 950 °C. The product of the synthesis was very sensitive to the temperature and gas flow rate as higher temperatures or gas flow rates could drive the full reduction of Fe²⁺ to Fe metal.

Laboratory X-ray diffraction for phase identification was carried out in a flat plate Bragg-Brentano geometry using a Bruker D8 Advance detector (217.5 mm radius) with a Cu K_α source and a 192-channel LynxEye detector with coarse energy sensitivity (~25%) that was used with

lower level (0.19 V) and window (0.06 V) settings that minimized sample fluorescence for Fe-containing samples. Synchrotron X-ray diffraction data were collected at the 11-BM beamline ($\lambda \sim 0.41 \text{ \AA}$) of the Advance Photon Source (APS) at Argonne National Laboratory with samples loaded in 0.8 mm diameter Kapton capillaries. Time-of-flight neutron diffraction data were collected at the POWGEN beamline of Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Different aliquots of the same ground powder sample were used for the equivalent X-ray and neutron experiments, as is ideal when co-refinements of data are to be carried out. The central wavelength for the time-of-flight neutrons was chosen to be $1.066 \text{ \AA}$, with a wavelength range of $0.533 \text{ \AA}$ to $1.599 \text{ \AA}$ and a minimum d -spacing of $\sim 0.28 \text{ \AA}$. Data were collected on samples packed in 6 mm vanadium cans. Rietveld refinement of diffraction data was done using the TOPAS v4.2 software package. In the combined refinement utilizing both neutron and X-ray diffraction data, the weighting scheme was adjusted so that X-ray and neutron data contributed equally to the weighted R value (R_{wp}) of the refinement. Although a geometrically correct absorption correction cannot presently be applied to the POWGEN data since a large number of different detector positions are utilized, an approximately correct empirical implementation of the standard cylindrical wavelength-dependent absorption correction was used that could estimate the sample linear absorption coefficient (μ_L) based on calibration against La^{11}B_6 data collected on the same instrument. Both these refined structures and literature structures were used as input for the calculation of bond valence sum (BVS) difference maps, using custom Fortran code that utilized the existing CrysFML library of crystallographic Fortran modules³⁴⁻³⁵. The resulting difference maps were displayed using the VESTA software package

RESULTS AND DISCUSSION

MgVBO₄

The element vanadium is well-suited for cathodes due to both the high voltage it typically generates, and the multiple oxidation states (3+, 4+ and 5+) that it can access in certain structures³⁷⁻³⁸. One large advantage of the use of divalent Mg^{2+} is that the number of mobile ions that need to be removed from the structure is halved relative to Li analogues, and enhanced specific capacities associated with accessing multiple valence states of vanadium can be realized even in compounds with equimolar amounts of mobile and redox-active cations. Thus the theoretical specific capacity of MgVBO_4 is very high (360 mAh/g). The complete removal of Mg^{2+} from MgVBO_4 will result in the oxidation state of V being increased from 3+ to 5+, though it is well known that the demagnesiation of structures is very challenging due to the poor mobility of Mg^{2+} and it is therefore expected that electrochemically driving the formation of VBO_4 from MgVBO_4 cathodes at room temperature will be difficult. The nature of the distribution of Mg and V over the two cation sites in the orthorhombic $M_2\text{BO}_4$ structure type can greatly impact the mobility of Mg^{2+} , and samples of MgVBO_4 were prepared in order to elucidate its structure through powder diffraction studies. This structural data is required for the estimation of Mg^{2+} diffusion path and the associated energy barriers through theoretical methods (such as DFT or bond valence sum difference maps).

The structure of MgVBO_4 was determined through the combined Rietveld refinement of synchrotron X-ray and time-of-flight neutron diffraction data using polycrystalline samples prepared at 1200 °C. Although time-of-flight neutron diffraction is by itself often sufficient to obtain accurate structural information, the scattering from V is almost completely incoherent, making V essentially invisible in neutron diffraction studies and necessitating more complex

combined Rietveld refinement with X-ray diffraction data in order to benefit from the sensitivity of neutrons to light atoms (B, O). Diffraction experiments were carried out on isotopically enriched $\text{MgV}^{11}\text{BO}_4$ samples instead of naturally abundant boron in order to avoid the severe neutron absorption of ^{10}B and the problems associated with this (for brevity, we will omit the isotopic identifier for our $\text{MgV}^{11}\text{BO}_4$ samples in the subsequent text).

The diffraction patterns of as-prepared MgVBO_4 was successfully indexed based on the orthorhombic space group ($Pnma$, #62) previously suggested for this phase²⁴⁻²⁵, with cell dimensions of $a = 9.25129(4)$ Å, $b = 3.10322(1)$ Å and $c = 9.36991(4)$ Å obtained through Rietveld refinement (Fig. 2). High quality diffraction data were obtained using both X-rays (satisfactory counting statistics to ~ 0.5 Å) and neutrons (~ 0.4 Å), allowing structural parameters for the atoms in MgVBO_4 to be accurately determined, as reported in Table 1. The use of two different types of radiation permits the simultaneous refinement of three different species (Mg^{2+} , V^{3+} , and vacancies) on the outer M_A and inner M_B cation sites. When a variety of structural models were tested, no evidence was found for cation vacancies in these refinements and the M_A and M_B sites were therefore constrained to be fully occupied in further modeling efforts. When the Mg and V occupancies were refined with this constraint, a stoichiometry of $\text{Mg}_{1.01}\text{V}_{0.99}\text{BO}_4$ was obtained. This refined stoichiometry does not significantly differ from the nominal sample composition, and the final refinement was therefore carried out with the cation sites constrained to conform to the ideal MgVBO_4 stoichiometry. When this constraint was applied, all atomic sites still exhibited displacement parameters that were generally reasonable for the type of element occupying the site. The outer M_A site had a Mg^{2+} occupancy of 79% while the inner M_B site had a V^{3+} occupancy of 79%, indicating the site preferences of these cations. Very similar Mg/V distributions and R_{wp} values were obtained regardless of whether the thermal parameters

of the M_A and M_B sites were constrained to be equal or were freely refined (as was done in the final refinement). While this data clearly indicates that Mg/V site disorder can be stabilized in a well-crystallized phase, it is not known if alternative thermal treatments (longer heating, different annealing temperatures, and/or rapid quenching) can be applied to eliminate this disorder, and the additional experiments needed to resolve this question are beyond the scope of the present work. The presence of site disorder is expected to be detrimental to both the electronic and ionic conductivity of this compound, though the sensitivity of the latter property will likely depend on the topology of the Mg^{2+} diffusion pathways.

Figure 2. Combined Rietveld refinement of a single sample of $\text{MgV}^{11}\text{BO}_4$ using synchrotron X-ray (top, $\lambda = 0.413695 \text{ \AA}$) and time-of-flight neutron (bottom) powder diffraction data. The modeled intensities (red line), difference pattern (gray line), and predicted reflection positions (green ticks) are superimposed on the data points (blue circles).

Table 1. Atomic coordinates and thermal parameters of MgVBO₄ (*Pnma*, #62)

Atom	Wyck.	x/a	y/b	z/c	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
M_A	4c	0.10289(5)	0.25	0.69044(5)	Mg = 0.791(2) V = 0.209(2)	1.35(5)
M_B	4c	0.11716(4)	0.25	0.06704(4)	Mg = 0.209(2) V = 0.791(2)	0.50(1)
B	4c	0.1668(1)	0.25	0.3735(1)	1	0.60(1)
O1	4c	0.0205(1)	0.25	0.3673(1)	1	0.46(1)
O2	4c	0.5098(1)	0.25	0.6158(1)	1	0.56(2)
O3	4c	0.2383(1)	0.25	0.5058(1)	1	0.49(1)
O4	4c	0.2473(1)	0.25	0.2476(1)	1	0.44(1)

The possibility of Mg removal from MgVBO₄ was tested through both chemical and thermal oxidation. However, no evidence for demagnesiumation prior to the thermal decomposition of MgVBO₄ was found in X-ray diffraction data or in TGA data (Figure S1) when this sample was heated. The room temperature chemical oxidation of MgVBO₄ was performed by immersing powders into a saturated aqueous K₂S₂O₈ solution (~0.2 M). Thermal oxidation was carried out both under flowing oxygen gas (TGA) and in ambient air in a box furnace (*ex situ* XRD data). The potassium persulfate solution has the advantage of a stronger electrochemical driving force for the demagnesiumation reaction (about 5 V *vs.* Li⁺/Li³⁹), while thermal oxidation has a very substantial kinetic advantage due to the elevated temperature. The fact that neither of these methods produces demagnesiumated MgVBO₄ suggests that the present disordered MgVBO₄ sample is not suitable for electrochemical storage applications, even in devices which utilize solid state electrolytes and can be run at elevated temperatures.

$Mg_xFe_{2-x}B_2O_5$

Although neither Mg₂B₂O₅ nor Fe₂B₂O₅ have the combination of mobile cations and redox active cations needed for battery functionality, these compounds share the same structure type^{19,21} and a solid solution of these two end members might be expected to form and to be suitable for electrochemical storage applications. Both a Fe-rich sample (Mg_{2/3}Fe_{4/3}B₂O₅, $x = 2/3$) and a Mg-rich sample (Mg_{4/3}Fe_{2/3}B₂O₅, $x = 4/3$) were prepared in ¹¹B-enriched forms to allow the use of neutron diffraction data to evaluate the possibility of Mg-removal from this structure type. The Fe-rich compound has a better possibility of achieving a Fe-percolating network within the ribbons that supports good electronic conductivity while the Mg-rich compound has a better possibility of forming a percolating network for ionic conductivity. The Fe-rich compound

$\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ has the highest theoretical capacity for one-electron Fe redox chemistry (186 mAh/g), with a hypothetical end product of " $\text{Fe}_{4/3}\text{B}_2\text{O}_5$ " after full oxidation of Fe^{2+} to Fe^{3+} , and is therefore the focus of the current study.

The $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ phases with both $x = 2/3$ and $x = 4/3$ could readily be prepared by solid state reaction, as evaluated from synchrotron X-ray diffraction patterns of the reaction products (Figure 3). The introduction of Fe into the $x = 2$ end member of $\text{Mg}_2\text{B}_2\text{O}_5$ clearly changed the intensity of the observed X-ray diffraction peaks, but did not alter the triclinic crystal system of $\text{Mg}_2\text{B}_2\text{O}_5$. The $x = 0$ end member of $\text{Fe}_2\text{B}_2\text{O}_5$ powder is more difficult to produce due to the need to control the Fe valence, and this compound was not prepared and evaluated in the course of this work. However, the lattice parameters of $\text{Fe}_2\text{B}_2\text{O}_5$ from a prior report were included in the current analysis²¹. As shown in Figure 3b, the unit cell volume of $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ decreases with increasing Mg content, as expected for the smaller ionic radius of Mg^{2+} (0.72 Å) relative to Fe^{2+} (0.78 Å), and this change is nearly linear in accord with expectations for constant cation volumes.

Figure 3. Left: Synchrotron diffraction patterns of $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ (red), $\text{Mg}_{4/3}\text{Fe}_{2/3}\text{B}_2\text{O}_5$ (green) and $\text{Mg}_2\text{B}_2\text{O}_5$ (blue), with $\lambda \sim 0.41 \text{ \AA}$. Right: Dependence of unit cell volume on cation fraction of Mg, defined as $[\text{Mg}] / ([\text{Mg}] + [\text{Fe}])$. The volume for $\text{Fe}_2\text{B}_2\text{O}_5$ was obtained from Ref. 21.

The structures of $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ and $\text{Mg}_{4/3}\text{Fe}_{2/3}\text{B}_2\text{O}_5$ were further investigated through the Rietveld refinement of time-of-flight neutron diffraction, which provides good sensitivity for all elements contained in these compounds (coherent scattering lengths in fm are Mg, 5.38; Fe, 9.45; ^{11}B , 5.30; O, 5.80) and which benefits from probing the more localized nucleus rather than the more delocalized electron cloud that X-rays are primarily sensitive to (Fig. 4). It was found that the $P\bar{1}$ structure previously determined for the end members of $\text{Mg}_2\text{B}_2\text{O}_5$ and $\text{Fe}_2\text{B}_2\text{O}_5$ was

effective for describing both the $x = 2/3$ and the $x = 4/3$ phases. The refinement and structural parameters obtained for these phases are given in Tables S1-4. When the mixed $\text{Mg}^{2+}/\text{Fe}^{2+}$ site occupancies and isotropic displacement parameters were freely refined, these ions were observed to be nearly randomly distributed between the M_A and M_B crystallographic sites in both $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ (0.37/0.30 vs. 0.33/0.33 for completely random mixing) and $\text{Mg}_{4/3}\text{Fe}_{2/3}\text{B}_2\text{O}_5$ (0.72/0.61 vs. 0.67/0.67 for completely random mixing). This is in contrast to the Mg/V distribution in MgVBO_4 , where Mg has a strong preference for occupying the M_A sites instead of the M_B sites in the 4-column ribbon framework. Since the M_A and M_B sites are crystallographically inequivalent in $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$, the only way that a truly random distribution of cations over the cation A and B sites can occur is if the free energy difference between the two configurations of $[\text{Fe}_A / \text{Mg}_B]$ and $[\text{Mg}_A / \text{Fe}_B]$ is exactly zero. However, the actual site occupancies will be experimentally indistinguishable from a completely random distribution if energy difference between these two configurations is small relative to kT at the synthesis temperature ($950^\circ\text{C} = 105\text{ meV}$), which might be expected to occur since the ionic radii and coordination preferences of these two divalent ions are similar. The best R -value for the refinement was obtained when structural model allowed partially disordered cations, and this R -value is significantly lower than that obtained when an fully ordered distribution of Mg and Fe is tested (R_{wp} of 5.326 vs. 5.718). However, a fully disordered mixture of Mg and Fe only produced a marginal increase in R_{wp} (from 5.326 to 5.330) relative to the partially disordered model. Therefore, we concluded that the Fe and Mg occupancies in the $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ phases are indistinguishable from the values expected for random mixing, and constrained the final refinement in this manner.

Figure 4. Rietveld refinement of $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ (bottom) and $\text{Mg}_{4/3}\text{Fe}_{2/3}\text{B}_2\text{O}_5$ (top) based on TOF neutron diffraction data (POWGEN).

The demagnesian of the $x = 2/3$ and $x = 4/3$ samples was attempted by both chemical and thermal oxidation. There was no evidence from color changes or from the lattice parameters determined from X-ray diffraction that aqueous persulfate ions were able to drive the removal of Mg from either structure at room temperature. However, the thermal oxidation of these samples induced substantial changes that suggested Mg removal is likely occurring. Preliminary analysis of a sample of intermediate composition (MgFeB_2O_5 , $x = 1$) by TGA and *ex situ* laboratory diffraction suggested that oxidation associated with demagnesian could occur without decomposition of the lattice over an approximate temperature range of 200 – 500 °C (Fig. S2).

More detailed structural studies were therefore carried out on the $x = 2/3$ and $x = 4/3$ samples heated at either 250 °C or 400 °C for 24 hours.

When analyzed, room temperature *ex situ* synchrotron X-ray diffraction data (Figure 5) on powder samples of $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ previously heated at 250 °C and 400 °C show clear shifts in peak positions (that are indicative of changing lattice parameters) and also large changes in diffraction peak intensities (that suggest substantial changes in site occupancies), two characteristic signatures that are expected to accompany demagnesiumation. These synchrotron X-ray diffraction patterns are also free of peaks from the Fe_2O_3 impurity phase that was found to be the eventual decomposition product at temperatures higher than 500 °C in our preliminary studies (Fig. S2), suggesting that the framework of $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ is preserved during oxidation at temperatures of 250 – 400 °C. All of the diffraction data therefore support the conclusion that the partial removal of Mg^{2+} ions (demagnesiumation) at these temperatures can occur without destruction of the $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ framework at intermediate temperatures of 250 – 500 °C.

When quantitatively fit in Rietveld refinements, the refined lattice parameters show that the unit cell volume decreases by 2.1% and 2.6% for samples treated at 250 °C and 400 °C, respectively. This decreased volume is expected for the demagnesiumation process as oxidation will result in both the removal of Mg^{2+} ions and in the oxidation of Fe^{2+} to Fe^{3+} , two changes which should both promote a reduction in unit cell volume. Additionally, it was observed that there was noticeable peak asymmetry in the 250 °C data, but not in the 400 °C data. The peak asymmetry is attributed to the skewed distribution of lattice parameters that results from the diffusion-limited inhomogeneous removal of Mg^{2+} ions at the lower temperature, and which is absent in the 400 °C sample, a temperature at which these ions have a greatly enhanced mobility.

Similar behavior in all aspects of diffraction was also observed for $\text{Mg}_{4/3}\text{Fe}_{2/3}\text{B}_2\text{O}_5$ samples (Figure S3).

Figure 5. Comparison of synchrotron X-ray diffraction pattern ($\lambda = 0.413695 \text{ \AA}$) for pristine $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ with patterns obtained after heating for 24 hours at 250 °C and 400 °C

A combined time-of-flight neutron and synchrotron X-ray diffraction study was carried out on the same 400 °C thermally oxidized sample of the $x = 2/3$ phase in order to precisely locate the light atoms (B and O) and to explicitly quantify the Mg content on the M_A and M_B sites in Rietveld refinements. The sample that was treated at 250 °C was not included in the present analysis due to the extra challenges associated with its asymmetric diffraction peaks. Lattice parameters for the 400 °C thermally oxidized sample were initially extracted through a Pawley fit using triclinic $P\bar{1}$ symmetry. However, the resulting triclinic lattice parameters of $a = 3.193(1) \text{ \AA}$, $b = 6.157(3) \text{ \AA}$, $c = 9.199(4) \text{ \AA}$, $\alpha = 104.983(4)^\circ$, $\beta = 90.096(8)^\circ$, and $\gamma = 90.030(9)^\circ$ do not substantially differ from those expected for monoclinic symmetry. Furthermore, a close

inspection of the high-resolution synchrotron X-ray diffraction pattern reveals that the ($h00$) reflections with odd h are missing, suggesting the presence of a two-fold screw axis along the a -axis of this $P\bar{1}$ cell. These observations are consistent with just two space group choices, $P2_1$ (#4) and $P2_1/m$ (#11). When the 400 °C oxidized structure was explored using the higher symmetry space group ($P2_1/m$), no chemically sensible structural model could be found. The final Rietveld refinement was therefore carried out using the space group $P2_1$, with the resulting structural parameters given in Tables S5 and S6 of the Supporting Information. The structural analysis indicates that the Mg cations from the M_B site are nearly completely depopulated during the thermal oxidation process while the M_A site remains fully occupied, indicating that about half of the theoretical capacity of 186 mAh/g is accessible at elevated temperatures. If these structural results are dominated by kinetic rather than thermodynamic consideration as might be expected for the temperature of this oxidation reaction, two conclusions can be inferred. First, the Mg ions on the M_B site are more mobile than those on the M_A site. Second, the diffusion of Mg ions at the M_B site is not significantly impeded by the coexistence of Fe on the same site. These conclusions are supported by our bond valence sum difference map analysis, as will be discussed later.

The loss of Mg^{2+} ions should also induce a change in the bond distances of the octahedral sites. While it is quite challenging to effectively obtain site occupancies when three species are mixed on a single site of this structure type (Mg, Fe, and vacancies), the bond distances obtained by Rietveld refinement should be insensitive to the nature of the central cation and thus provide an independent mechanism of following the changes in the crystal structure that occur on heating. When the 400 °C sample is compared with the pristine sample, the average bond distance for the M_A site is reduced by 0.06 Å (from 2.134 to 2.087 Å), while the M_B site average distance is

reduced by 0.03 Å (from 2.149 to 2.118 Å). The substantially larger reduction of bond distances on the M_A site suggests that the oxidation of Fe^{2+} to Fe^{3+} occurs primarily on this site.

Figure 6. Combined Rietveld refinement of (top) TOF neutron and (bottom) synchrotron X-ray diffraction data for a $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ sample that was annealed at 400 °C in air for 1 day, resulting in a final refined composition of $\text{Mg}_{0.36}\text{Fe}_{1.33}\text{B}_2\text{O}_5$.

Mg^{2+} diffusion pathway

Insights into Mg^{2+} diffusion were obtained through bond valence sum difference maps. Since the BVS difference map method has not previously been applied to Mg-ion batteries, some comparative calculations were also carried out on a few other known or hypothesized Mg-ion battery cathode materials. FePO_4 , the delithiated form of olivine LiFePO_4 , has been recently proposed as a cathode material for Mg-ion battery applications based on the relatively high

voltage calculated for this system in DFT calculations⁴⁰. However, no estimate of the kinetic barriers to Mg-ion diffusion was made as a part of that work. The BVS difference map calculated for this compound (Figure 7a) forms a percolating network with a very low threshold ($|\Delta V| < 0.1$ v.u.), suggesting that there are no structural barriers to diffusion within this framework, with the same diffusion pathway topology (1D diffusion path along *b*-axis) predicted for both Mg^{2+} and Li^+ ⁴¹. This compound should be therefore considered as a promising candidate battery cathode in which Mg-ion diffusion might be observed at or near room temperature.

Figure 7. Bond valence sum difference maps (and $|\Delta V|$ thresholds used in their construction) for FePO_4 (0.1 v.u.), MgMnSiO_4 (0.3 v.u.), and Mo_6S_8 (1.7 v.u.). These maps were calculated for Mg^{2+} using the soft BVS parameters previously determined for O^{2-} (FePO_4 , MgMnSiO_4) or S^{2-} (Mo_6S_8).

A second olivine-type compound of MgMnSiO_4 was also investigated. In contrast to the almost perfect ordering of Li and Fe between the two available octahedral sites in the Li-containing olivine structural framework, Mg and Mn are partially disordered resulting in a 73/27

distribution of cations with the Mn ions preferentially occupying the site analogous to that of Li in LiFePO_4 ⁴². Based on the BVS map (Fig. 7b), it is expected that Mg^{2+} diffusion occurs through a pathway that connects both the primary and minority octahedral sites in which Mg can be found. The threshold $|\Delta V|$ barrier for establishing a Mg^{2+} percolation pathway is 0.3 v.u. Since the topology of the minimal percolation network requires access to both types of octahedral sites, this pathway is expected to be effectively blocked by the immobile Mn cations in both the majority and minority sites, making it likely that the actual barrier to diffusion is much higher than that suggested by the percolation threshold of 0.3 v.u.

The Chervrel phase Mo_3S_4 is perhaps the only well-established cathode material for Mg-ion battery applications⁷. Despite the experimentally observed mobility of Mg^{2+} ions at room temperature, the BVS method does not predict that this framework will support Mg-ion diffusion as the percolation threshold is $|\Delta V| > 1.7$ v.u. (Fig. 7c). This Chevrel phase structure differs from that of most solid state compounds in that it consists of Mo_6S_8 clusters with many strong internal covalent bonds, but without rigid S-S covalent bonds connecting neighboring clusters (the shortest S-S bond length is ~ 3.3 Å). This suggests that the Chevrel framework can be much more readily distorted than the hard oxide or oxoanion framework of conventional Li-ion battery systems, and that the static structural snapshot used for BVS calculations is inadequate for making accurate predictions if large dynamic structural changes occur in response to the intercalation and de-intercalation of ions. Given the difficulty in identifying rigid oxide frameworks that permit Mg^{2+} ion mobility at room temperature, it is perhaps appropriate to devote additional efforts to identifying and evaluating structures with “soft” modes for their suitability for Mg-ion electrodes.

The potential for the frameworks of $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ and MgVBO_4 to support Mg-ion diffusion can be evaluated in the context of these baseline investigations. The MgVBO_4 map calculated for MgVBO_4 does not reach the percolation limit until an extremely high threshold of about 1.2 v.u. is passed, indicating that Mg^{2+} ions are essentially immobile within this structure (Fig. 8). Furthermore, the BVS-predicted pathway for hopping from one octahedral site to another involves crossing directly in between two borate group triangles, which will result in Mg^{2+} ions passing between two B atoms that are only 3.1 Å apart (Fig. 8b). Since electrostatic repulsions are not included in BVS calculations, the true barrier for Mg-ion diffusion will be much larger than that estimated using the BVS method. As a result, it can be concluded that Mg^{2+} ions will be fully immobilized both at room temperature and at elevated temperatures. Given the unfavorable diffusion network topology of MgVBO_4 , it is improbable that the diffusion of Mg^{2+} can be enabled by chemical substitution, and this general structure type should not be investigated further for applications requiring Mg^{2+} diffusion (intercalation-type batteries, solid state electrolytes, *etc.*). More generally, it can be concluded that it is highly unfavorable for Mg ions to diffuse directly between octahedra which share an edge, and that alternate external diffusion pathways must exist in order to achieve Mg-ion mobility in structures with ribbons of edge-sharing octahedra.

Figure 8. Bond valence sum difference maps for MgVBO_4 shown for $|\Delta V|$ threshold of 1.2 v.u., reflecting the predicted immobility of Mg^{2+} ions in this framework.

While the orthoborate framework of MgVBO_4 greatly inhibits Mg-ion diffusion, the analogous ribbon structure of pyroborate $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ has a nearly ideal topology that results in a defect-tolerant pathway for Mg-ion diffusion enabled by the different geometric pattern in which the quadruple octahedral ribbons are arranged. As seen in Fig. 9, there are two types of interstitial defect sites (I_A and I_B) which are predicted to readily accommodate Mg^{2+} ions that have hopped out of their original octahedral sites. Each defect site can be readily accessed from just two neighboring octahedral cation sites which are of the same type (both M_A or both M_B), and these two defect sites are therefore labeled as I_A and I_B . The I_A interstitial sites linking pairs of M_A cations have a strongly skewed rectangular arrangement of oxygen anions at their corners, while the I_B interstitial sites linking pairs of M_B cations form a more regular rectangular environment

that is expected to be more accessible to Mg^{2+} ions based on geometric considerations. Indeed, the more open nature of I_B sites allows them to be connected into a one-dimensional (1D) channel permitting Mg-ion diffusion parallel to the ribbons (a -axis direction) at a much lower valence threshold (0.2 v.u.) than the I_A sites (0.5 v.u.) based on the BVS difference map analysis.

Figure 9. Bond valence sum difference maps (and $|\Delta V|$ threshold used in the construction) for $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ (0.2 v.u.). When the BVS map is viewed along the a -axis direction, it can be seen that no percolation diffusion path exists within the bc plane. In the unit cell of $\text{Mg}_{2/3}\text{Fe}_{3/4}\text{B}_2\text{O}_5$, as highlighted by the black dotted lines in (a), three types of interstitial defect sites are present (I_A , I'_A and I_B). The I_A and I_B sites are likely accessible to Mg^{2+} ions that are on the M_A and M_B octahedral sites, respectively. As shown in (b) and (c), only I_B sites which connect the M_B crystallographic site form a 1D percolation channel at a low threshold of ~ 0.2 v.u. The Mg^{2+} conduction pathways should be very tolerant to disorder, as schematically

illustrated in (d). In analogy to a parking lot, Mg^{2+} ions are “parked” in octahedral sites until thermally excited into the interstitial sites corresponding to the aisles of the parking lot. The ions can then travel freely through the interstitial sites in the aisles, and are therefore unaffected by the Mg/Fe disorder on the octahedral sites that correspond to parking spots.

When viewed from the side, it can be seen that these 1D channels appear to be completely tolerant to the presence of defects on the octahedral sites (Fig. 9c). These channels form aisles like those in a parking lot, in which Mg^{2+} ions are typically “parked” in octahedral sites (Fig. 9d). However, once the Mg^{2+} ions pull out of their parking spots, they can move continuously through these aisles without having to enter another octahedral site. Therefore, the presence of Fe^{2+} or Fe^{3+} ions in the other parking spots will not inhibit the facile diffusion of Mg^{2+} ions through the aisles. Of course, if the Fe ions do leave their parking spot and enter the aisle, they will have the ability to limit the diffusivity of Mg ions in these channels, though it is expected to be relatively easy for Fe ions in the aisle to re-enter a parking spot, making these blockages transient. While the presence of site disorder is known to have a strongly deleterious effect on the conductivity of mobile ions in olivine battery cathodes such as LiFePO_4 ⁴³, the mobility of Mg^{2+} ions in the pyroborate structure of $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ should be negligibly affected by Mg/Fe disorder on the octahedral cation sites. This should be a general characteristic of structures whose primary diffusion pathway is through interstitial sites.

It should be noted that the achievable capacity of $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ cathodes will be affected by the proportion of Mg ions on the M_A and M_B sites. The structural refinement of demagnesiased $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ sample prepared by thermal oxidation at 400 °C indicates that Mg ions are removed from the M_B site and not the M_A site. This general conclusion is robust (large amounts of Mg are removed from the M_B site), although the general limitations of working with powder

diffraction data and the specific uncertainty associated with the fraction of Fe ions on the M_A and M_B sites possibly changing during the thermal treatment (due to the likely mobility of Fe at these elevated temperature) make it impossible for us to rule out the loss of small amounts of Mg from the M_A site. The refinements indicate that thermal energy at modest temperatures of 250 – 400 °C is sufficient to enable Mg-ion motion through the I_B site, but is not sufficient to permit Mg-ions to access the I_A site. As a result, the Mg ions from the M_A site will not contribute to the achievable specific capacity of this framework. The two best pathways for improving the performance of the pyroborate framework are (1) chemical substitutions that improve the mobility of Mg^{2+} ions travelling through the I_B interstitial site in this structure, and (2) thermal treatments or chemical substitutions that result in a larger number of Mg cations on the M_B octahedral site, enhancing the specific capacity.

CONCLUSIONS

Two classes of borates with quadruple octahedral ribbons were investigated for their suitability as Mg-ion battery cathodes due to their high theoretical capacity for this application. The orthoborate $MgVBO_4$ and the pyroborate $Mg_xFe_{2-x}B_2O_5$ compounds were synthesized by solid state methods and their structures were for the first time accurately determined through the Rietveld refinement of synchrotron X-ray and time-of-flight neutron diffraction data. In both compounds, there are two distinct types of octahedral sites – the M_A site at the edge of the quadruple ribbons and the M_B site at the center of the quadruple ribbons. Both experimental (attempted chemical and thermal oxidation) and theoretical (bond valence sum difference maps) analyses suggest that Mg ions are fully immobilized in $MgVBO_4$ over the full range of temperatures over which this framework is stable (below ~450 °C). In contrast, it is

experimentally demonstrated that Mg-ions can be removed from $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ ($x = 2/3, 4/3$) by thermal oxidation over an approximate temperature range of 200 – 500 °C. BVS difference maps analysis indicates that the preferred diffusion pathway for Mg^{2+} ions is through interstitial spaces which are paired with the inner M_B octahedral sites, and it is confirmed through Rietveld refinements that only the Mg^{2+} ions at this site are selectively depopulated during thermal oxidation. This validates the use of BVS difference maps method as a predictive tool for understanding Mg-ion diffusion. The topology of this interstitial diffusion pathway resembles that of the aisle in a parking lot and therefore makes this pathway insensitive to disorder (Mg/Fe mixing) on the M_B octahedral site, allowing extra flexibility in future efforts to improve the Mg-ion mobility in this structure by chemical substitution. Although the pyroborate $\text{Mg}_x\text{Fe}_{2-x}\text{B}_2\text{O}_5$ compounds do not have mobile Mg^{2+} ions at room temperature, their ability to transport Mg^{2+} ions at modest temperatures (~250 °C) is a promising advance given the current lack of oxide structures with the ability to reversibly intercalate Mg-ions at room temperature or conduct Mg^{2+} at intermediate temperature range. Based on the BVS analysis, it is expected that both the present pyroborate and the well-known olivine structure types have good potential for supporting Mg-ion diffusion at or near room temperature with appropriate chemical substitution, and merit future investigations as cathodes and solid state electrolytes for Mg-ion battery applications.

ASSOCIATED CONTENT

Supporting Information.

Additional information about the chemical demagnesiumation of MgVBO_4 , TOF neutron diffraction studies of $\text{Mg}_{2/3}\text{Fe}_{4/3}\text{B}_2\text{O}_5$ and $\text{Mg}_{4/3}\text{Fe}_{2/3}\text{B}_2\text{O}_5$, preliminary results for the demagnesiumation of

"MgFeB₂O₅", and structural information about demagnesiased Mg_{2/3}Fe_{4/3}B₂O₅. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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