

Supporting Information

Borate-based Compounds as Mixed Polyanion Cathode Materials for Advanced Batteries

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Table S1. Model metal-BPO compounds and the suggested synthetic routes to obtain earth-abundant metal target isostructures.

| Model Structures | Structure Description | Target Isostructure | Suggested Synthetic Routes | Reference |
|---|--|--|---|-----------|
| M[BPO ₄ (OH) ₂] M = Mn, Fe, Co | A 3D structure formed by edge-sharing helical MO ₆ chains wound around 3 ₁ or 3 ₂ screw axes interconnected by BPO single chains of alternating BO ₂ (OH) ₂ and PO ₄ tetrahedra | Ni[BPO ₄ (OH) ₂] | Hydrothermal method: $\text{NiCl}_2 \cdot 4\text{H}_2\text{O} + \text{H}_3\text{BO}_3 + \text{DABCO} + \text{H}_3\text{PO}_4 \xrightarrow[170\text{ }^\circ\text{C H}_2\text{O}]{}$ Ni[BPO ₄ (OH) ₂] DABCO = 1,4-diazobicyclo[2.2.2]octane | [1] |
| Fe ₂ BP ₃ O ₁₂ | A 3D network formed by BO ₃ triangular planar structures corner sharing three PO ₄ tetrahedra to form a zero-dimensional (0D) anionic unit of [BP ₃ O ₁₂] ⁶⁻ . The BPO units are further connected by the FeO ₆ . | Ni ₂ BP ₃ O ₁₂ | Flux method $\text{Cs}_2\text{CO}_3 \text{ (flux)} + \text{H}_3\text{BO}_3 + \text{NH}_4\text{H}_2\text{PO}_4 + \text{NiO} \xrightarrow[850\text{ }^\circ\text{C H}_2\text{O}]{}$ Ni ₂ BP ₃ O ₁₂ | [2] |
| (Co _{0.6} Mn _{0.6}) ₂ (H ₂ O)[BP ₃ O ₉ (OH)] | Isostructural phases constructed from infinite chains of alternately connected distorted M ^{II} O ₄ (OH)(H ₂ O) and M ^{II} O ₅ (OH) octahedra. The M ^{II} chains are interconnected by BPO tetrahedra, resulting in a 3D framework structure. | M ₂ (H ₂ O)[BP ₃ O ₉ (OH) ₄] | Hydrothermal method: | [3] |
| Mg ₂ (H ₂ O)[BP ₃ O ₉ (OH) ₄] | | | $\text{M}(\text{OH})_2 + \text{H}_3\text{BO}_3 + \text{H}_3\text{PO}_4 \xrightarrow[190\text{ }^\circ\text{C H}_2\text{O}]{}$ M ₂ (H ₂ O)[BP ₃ O ₉ (OH) ₄] | [4] |
| Co ₅ BP ₃ O ₁₄ | The structure is composed of triangular planar BO ₃ corner sharing PO ₄ tetrahedra forming BPO ₆ ⁴⁻ dimers. Layers of the dimers are separated by double layers of isolated PO ₄ tetrahedra. There are five Co sites in the structure joining the BPO layers together | M ₅ BP ₃ O ₁₄ M = Fe, Ni | High-Temperature Flux Method: $\text{MCO}_3 \cdot x\text{H}_2\text{O} + \text{B}_2\text{O}_3(\text{flux}) + \text{H}_3\text{PO}_4 \xrightarrow[950\text{ }^\circ\text{C}]{}$ M ₅ BP ₃ O ₁₄ | [5] |
| Cu[B ₂ P ₃ O ₁₂ (OH) ₃] | The 3D framework is composed of a BPO chain formed by corner-sharing borate and phosphate tetrahedra in 4-membered tetrahedral rings and a Cu zigzag chain in alternating trigonal bipyramid and octahedral coordination. The chains are alternately stacked forming a parallel rod stacking matrix. Additional PO ₄ tetrahedron are found in between the copper polyhedral chains further joining the structure. | M[B ₂ P ₃ O ₁₂ (OH) ₃] M = Fe, Ni | Hydrothermal method: $\text{MCl}_2 \cdot x\text{H}_2\text{O} + \text{H}_3\text{BO}_3 + \text{NH}_4\text{H}_2\text{PO}_4 \xrightarrow[170\text{ }^\circ\text{C H}_2\text{O}]{}$ M[B ₂ P ₃ O ₁₂ (OH) ₃] | [6] |

| | | | | |
|---|--|---|--|------|
| Zn[BPO ₄ (OH) ₂] | An open framework structure built from unbranched vierer-single BPO chains. The chains are interconnected by Zn tetrahedra to form a 3D structure | M[BPO ₄ (OH) ₂] M = Fe, Ni | Hydrothermal method: | [7] |
| | | | $\text{MO} + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5 \xrightarrow{170\text{ }^\circ\text{C H}_2\text{O}}$ | |
| LiCu ₂ BP ₂ O ₈ (OH) ₂ | An open framework structure built up of layers formed by BO ₄ and PO ₄ tetrahedra joined together by CuO ₆ and LiO ₆ . The Li lies in a center of symmetry. | LiM ₂ BP ₂ O ₈ (OH) ₂ M = Fe, Ni | Hydrothermal method: | [8] |
| | | | $\text{M}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} + \text{Li}_2\text{B}_4\text{O}_7 + \text{H}_3\text{PO}_4 \xrightarrow{170\text{ }^\circ\text{C H}_2\text{O}}$ | |
| Na ₅ (H ₃ O) {M ₃ [B ₃ O ₃ (OH)] ₃ (PO ₄) ₆ ·2H ₂ O M = Mn, Co, Ni | An open framework structure built up of layers formed by BO ₄ and PO ₄ tetrahedra joined together by CuO ₆ and LiO ₆ . The Li lies in a center of symmetry. | Na ₅ (H ₃ O){Fe ₃ [B ₃ O ₃ (OH)] ₃ (PO ₄) ₆ ·2H ₂ O | Hydrothermal method: | [9] |
| | | | $\text{FeCl}_2 \cdot x\text{H}_2\text{O} + \text{H}_3\text{BO}_3 + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \xrightarrow{200\text{ }^\circ\text{C H}_2\text{O}}$ | |
| | | Na ₅ (H ₃ O){Fe ₃ [B ₃ O ₃ (OH)] ₃ (PO ₄) ₆ ·2H ₂ O | | |
| NaFe[BP ₂ O ₇ (OH) ₃] | A 3D structure is formed by metal phosphate Kagome lattice layers are joined together by triborates. The 3D framework forms channel structures joined by MO ₆ . Na ⁺ reside in pockets in the structure. | NaNi[BP ₂ O ₇ (OH) ₃] | Hydrothermal method: | [10] |
| | | | $\text{NiCl}_2 \cdot x\text{H}_2\text{O} + \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{170\text{ }^\circ\text{C H}_2\text{O}}$ | |
| | | NaNi[BP ₂ O ₇ (OH) ₃] | | |
| CaCo(H ₂ O)[BP ₂ O ₈ (OH)]·H ₂ O | Structure is built on isolated BPO anions joined by Fe octahedrons. Na ⁺ is 8-fold coordinated to O forming cubes. | MgM(H ₂ O)[BP ₂ O ₈ (OH)]·H ₂ O M = Fe, Ni | Hydrothermal method: | [11] |
| | | | $\text{Mg}(\text{OH})_2 + \text{M}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O} + \text{B}_2\text{O}_3 + \text{H}_3\text{PO}_4 \xrightarrow{170\text{ }^\circ\text{C H}_2\text{O}}$ | |
| | | MgM(H ₂ O)[BP ₂ O ₈ (OH)]·H ₂ O | | |
| CaFe[BP ₂ O ₇ (OH) ₃] | Layers built of BPO oligomers, interconnected by Co octahedra. Inter-layer connections are by Ca octahedra. | MgFe[BP ₂ O ₇ (OH) ₃] | Hydrothermal method: | [12] |
| | | | $\text{Mg}(\text{OH})_2 + \text{FeCl}_2 \cdot x\text{H}_2\text{O} + \text{B}_2\text{O}_3 + \text{H}_3\text{PO}_4 \xrightarrow{170\text{ }^\circ\text{C H}_2\text{O}}$ | |
| | | MgFe[BP ₂ O ₇ (OH) ₃] | | |

Table S2. Model metal-BSiO compounds and the suggested synthetic routes to obtain earth-abundant metal target isostructures.

| Model Structures | Structure Description | Target Isostructure | Suggested Synthetic Routes | Reference |
|--|---|---|---|-----------|
| NaCa ₅ BO ₃ (SiO ₄) ₂ | A tangled 3D network of isolated BO ₃ triangles and SiO ₄ tetrahedra. Calcium bonds with 7-9 oxygen atoms which build up the 3D Ca-O framework | NaM ₅ BO ₃ (SiO ₄) ₂ M = Fe, Ni | Solid-state method $\text{Na}_2\text{CO}_3 + \text{MCO}_3 + \text{B}_2\text{O}_3 + \text{SiO}_2 \xrightarrow{890^\circ\text{C}} \text{NaM}_5\text{BO}_3(\text{SiO}_4)_2$ | [13] |
| CaBSiO ₅ H | Layers of B-Si-O networks connected by Ca atoms. SiO ₄ and BO ₃ (OH) tetrahedra form the BSiO ₄ (OH) apophyllite layers with four- and eight- membered loops | MBSiO ₄ (OH) M = Fe, Ni | Hydrothermal method $\text{MO} + \text{B}_2\text{O}_3 + \text{SiO}_2 \xrightarrow{250^\circ\text{C H}_2\text{O}} \text{MBSiO}_4(\text{OH})$ | [14] |
| BaB ₂ Si ₂ O ₈ | A 3D structure of Si ₂ O ₇ and B ₂ O ₇ diortho groups that form the Si ₂ B ₂ O ₈ anorthite-like framework | MB ₂ Si ₂ O ₈ M = Fe, Ni | Solid-state method $\text{MCO}_3 + \text{H}_3\text{BO}_3 + \text{SiO}_2 \xrightarrow{850^\circ\text{C}} \text{MB}_2\text{Si}_2\text{O}_8$ | [15] |

Table S3. Model metal-BSO compounds and the suggested synthetic routes to obtain earth-abundant metal target isostructures.

| Model Structures | Structure Description | Target Isostructure | Suggested Synthetic Routes | Reference |
|---|--|--|--|-----------|
| M[B ₂ (SO ₄) ₄] M = Mg, Co | <p>α-M[B₂(SO₄)₄] - Comprises of infinite anionic layers consisting of alternating, corner sharing borate and sulfate tetrahedra. Each borate tetrahedron is bonded to adjacent sulfate tetrahedra while the sulfate tetrahedra have two borate bridging oxygen atoms and two terminal oxygen atoms. The BSO layers are joined together by octahedral binding M.</p> <p>β-M[B₂(SO₄)₄] - Consists of alternating corner-sharing borate and sulfate tetrahedra that form a layer of adjacent Vierer and Zwölfer rings. M ions are found on the corners and at the centre of the unit cell bound octahedrally within the Zwölfer ring and with two oxygen atoms from adjacent layers.</p> | M[B ₂ (SO ₄) ₄] M = Fe, Ni | <p>Solvothermal method:</p> $\text{M}(\text{CO}_3)_3 \cdot x\text{H}_2\text{O} + \text{B}_2\text{O}_3 + \text{H}_2\text{SO}_4 \xrightarrow{180\text{ }^\circ\text{C}} \text{M}[\text{B}_2(\text{SO}_4)_4]$ | [16] |
| (H ₃ O)Bi[B(SO ₄) ₂] ₄ | Consists of all-corner sharing borate and sulfate supertetrahedra forming a 3D network. Vierer and Achter rings are found in the structure forming channels. The Vierer ring channels host the bismuth, while the Achter ring channels the H ₃ O ⁺ . | NaM[B(SO ₄) ₂] ₄ M = Fe, Ni | <p>Solvothermal method:</p> $\text{NaCl} + \text{MCl}_3 \cdot x\text{H}_2\text{O} + \text{H}_3\text{BO}_3 + \text{H}_2\text{SO}_4 \xrightarrow{200\text{ }^\circ\text{C}} \text{NaM}[\text{B}(\text{SO}_4)_2]_4$ | [17] |
| M ₄ [B ₂ O(SO ₄) ₆] M = Mg, Mn, Co, Ni, Zn | <p>α-M₄[B₂O(SO₄)₆] - Comprises of layers of open-branched quadruple tetrahedra edge-sharing [B₂O(SO₄)₆]⁸⁻ anions. The BSO layers are joined by the octahedra forming M₂O₉ face-sharing dimers forming a 3D network.</p> <p>β-M₄[B₂O(SO₄)₆] - Comprises the same fundamental building units as the α-polymorph; however, the BSO moieties alternate between staggered and eclipsed conformations</p> | Fe ₄ [B ₂ O(SO ₄) ₆] | <p>Solvothermal method:</p> $\text{H}[\text{B}(\text{HSO}_4)_4] + \text{FeO} \xrightarrow{200\text{ }^\circ\text{C}} \text{Fe}_4[\text{B}_2\text{O}(\text{SO}_4)_6]$ | [18] |

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