Probing Capacity Trends in MLi$_2$Ti$_6$O$_{14}$ Lithium-Ion Battery Anodes Using Calorimetric Studies

K. Jayanthi, Anshuman Chaupatnaik, Prabeer Barpanda, and Alexandra Navrotsky

ABSTRACT: Due to higher packing density, lower working potential, and area specific impedance, the MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) titanate family is a potential alternative to zero-strain Li$_4$Ti$_5$O$_{12}$ anodes used commercially in Li-ion batteries. However, the exact lithiation mechanism in these compounds remains unclear. Despite its structural similarity, MLi$_2$Ti$_6$O$_{14}$ behaves differently depending on charge and size of the metal ion, hosting 1.3, 2.7, 2.9, and 4.4 Li per formula unit, giving charge capacity values from 60 to 160 mAh/g in contrast to the theoretical capacity trend. High-temperature oxide melt solution calorimetry measurements confirm strong correlation between thermodynamic stability and the observed capacity. The main factors controlling energetics are strong acid–base interactions between basic oxides MO, Li$_2$O and acidic TiO$_2$, size of the cation, and compressive strain. Accordingly, the energetic stability diminishes in the order Na$_2$Li$_2$Ti$_6$O$_{14}$ > BaLi$_2$Ti$_6$O$_{14}$ > SrLi$_2$Ti$_6$O$_{14}$ > PbLi$_2$Ti$_6$O$_{14}$. This sequence is similar to that in many other oxide systems. This work exhibits that thermodynamic systematics can serve as guidelines for the choice of composition for building better batteries.

INTRODUCTION

Lithium-ion batteries (LIBs) are currently favored power sources for portable applications such as electric vehicles and electronic products. Most commercial LIBs work via reversible intercalation of lithium ions between a (mixed) transition metal oxide cathode and a layered graphite anode. For more than 30 years since the inception of LIBs by SONY (Tokyo, Japan) in the 1990s, graphite remains the most widely used and optimized anode material due to its high theoretical capacity (380 mAh/g) and low Li insertion voltage (ca. 0.2 V) while maintaining an intercalation mechanism, which guarantees structural integrity and long cycle life. Nevertheless, the graphite anode has several issues, such as solvent-dependent stability, large volume change, large irreversible capacity loss (ICL) from solid electrolyte interphase (SEI) formation (below 0.8 V), and fire risk due to lithium plating during overcharge or higher currents some of which directly stem from its low voltage performance.

In this context, the zero-strain spinel Li$_4$Ti$_5$O$_{12}$ anode operating at flat and higher voltage (1.55 V vs Li, 175 mAh/g) was introduced and is commercially preferred over graphite in applications requiring fast charging and safety. Additionally, Li$_4$Cr$_2$Ti$_3$O$_{12}$ similar to Li$_4$Ti$_5$O$_{12}$ spinel synthesized at 800 °C exhibits large charge capacity, good cycle stability, superior rate performance, and outstanding electrochemical kinetics. When cycled at 200 mAh/g, it displays a high initial reversible capacity of 146.6 mAh/g and retains a considerable capacity of 130.8 mAh/g after 300 cycles. Among other Ti-based electrode materials, MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) shows lower voltage (1.28–1.42 V vs Li), low area specific impedance, and higher packing density than Li$_4$Ti$_5$O$_{12}$ and has a high theoretical capacity (220–282 mAh/g) for redox activity of all six Ti (Figure 1i). The MLi$_2$Ti$_6$O$_{14}$ series exhibit open channels enabling reversible Li$^+$ insertion in vacant sites like 8c, 4a, and 4b of the orthorhombic framework (Cmca). However, the observed capacity trend in this series does not follow the theoretical capacity trend. Previous studies identified crystallographic origins underlying the low capacity of the monovalent member (M = 2Na) vs the divalent members (M = Ba, Sr, and Pb). However, currently there is no explanation of the anomalous trend of the observed capacity in the isostructural MLi$_2$Ti$_6$O$_{14}$ series from their relative thermodynamic stabilities, attempting to elucidate the structure–property relationships in this family of materials. High-temperature oxide melt solution calorimetry is an established methodology to measure the thermodynamic stabilities of oxide and nonoxide systems. Recently, Abramchuk et al. used this method to investigate the thermodynamic stability and its role in the mechanism of ionic...
transport in the NASICON-type solid-state electrolyte Li$_{1+x}$Al$_{1-x}$Ti$_2$O$_{22}$ (PO$_4$)$_3$. They demonstrated a strong correlation between the energetic stability and ionic conductivity in LATPs with a pronounced change in the trends with composition. In the present work, we employ high-temperature oxide melt solution calorimetry to systematically assess the thermodynamic stability of MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb), which provides insights into observed differences in the capacity. We found a strong correlation between the thermodynamic stability and reversible lithium insertion in MLi$_2$Ti$_6$O$_{14}$ anode materials and explain the trend in observed capacity. This work reflects the acid–base energetic contributions in this class of anode materials.

**EXPERIMENTAL SECTION**

**Synthesis and Electrochemistry.** MLi$_2$Ti$_6$O$_{14}$ was synthesized by a two-step solution combustion method. Metal nitrates as oxidizers (O) and glycine as fuel (F) were taken in a 1:1 ratio to ensure maximum exothermicity. Lithium nitrate (LiNO$_3$, Sigma-Aldrich, 99%), sodium nitrate (NaNO$_3$, SD Fine, 99.5%), barium nitrate (Ba(NO$_3$)$_2$, Sigma-Aldrich, 99%), lead nitrate (Pb(NO$_3$)$_2$, SD Fine, 99.5%), and strontium nitrate (Sr(NO$_3$)$_2$, Sigma-Aldrich, 99%) were used. Titanium (Ti$^{4+}$) ions were sourced from freshly prepared titanyl nitrate (TiO(NO$_3$)$_2$, Sigma-Aldrich, 97%) in isopropyl alcohol.

![Figure 1.](http://pubs.acs.org/journal/acsodf)

(a–d) Rietveld refinement of XRD (Cu Ka) patterns of members of the MLi$_2$Ti$_6$O$_{14}$ family (M = 2Na, Sr, Ba, and Pb) formed by solution combustion (900 °C, 2 h). Experimental data points (gray dots), calculated pattern (black), their difference (blue), and Bragg reflections (black bars) of the respective isostructural phases are shown. (e–h) SEM micrographs of the combustion synthesized MLi$_2$Ti$_6$O$_{14}$ anode indicating porous structure of secondary agglomerates. The inset shows a TEM image of primary nanometric particles (200 nm scale). (i) Structural illustration of the MLi$_2$Ti$_6$O$_{14}$ anodes. (j–m) Galvanostatic (dis)charge voltage profiles and (n–q) differential capacity plots depicting the electrochemical performance of the MLi$_2$Ti$_6$O$_{14}$ anodes.

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(Merck, analytical grade 99.7%) under ice-cold conditions. The mixture was heated to less than 150 °C to remove water and form a thick solution, which was reheated at 500 °C to trigger combustion. The resulting white intermediate powder was ground, pelletized, and annealed in air at 900 °C for 1 min to 2 h. The phase purity of combustion prepared MLi2Ti6O14 samples was verified from powder X-ray diffraction patterns (2θ range = 10–50°, step size = 0.026° s–1) obtained using a PANalytical X’Pert Pro X-ray diffractometer having a Cu-Kα source (λ = 1.54 Å). Rietveld refinement was done using the GSAS program. The structures were illustrated using the VESTA software.26

The surface morphology of the powders was characterized using a scanning electron microscope having a LaB6 field emission source (Carl Zeiss ULTRASS FESEM, 5 kV) and using a transmission electron microscope (FEI Tecnai F20 STwin, 200 kV). TG-DSC measurements were performed using a Setaram AlexSYS Tian-Calvet twin microcalorimeter. High-temperature oxide melt solution calorimetry was performed using a Neware BTS-4000 battery cycler to ensure we reach the maximum specific capacity values for each of the materials, which can then be rationalized with the thermodynamic trend.

### RESULTS AND DISCUSSION

#### Structure and Electrochemical Performance.

The combustion synthesized MLi2Ti6O14 powders were found to be phase pure from Rietveld refinement (Figure 1a–d and Tables S1–S4, Supporting Information). The powders were well crystallized into primary particles of about 1 micron, which agglomerated to a porous network (Figure 1e,f). The crystal structure is orthorhombic (symmetry: Cmca), containing a three-dimensional network of TiO6 octahedral units. Two edge-shared units along the b-axis stitch the infinite c-axis directed edge-shared units in a ladderlike way. The ladders form a sheet in the bc plane. In the sheet, inside each c-directed ladder, there is an empty tunnel where structural lithium ions sit in tetrahedral sites with adjacent octahedral sites free. This sheet is three units thick along the a-axis and is glued to other sheets via larger M ions which populate the interlayer partially (M = Sr, Ba, and Pb) or completely (M = 2Na). One unit of MLi2Ti6O14 can host up to six lithium atoms, for complete reduction of Ti4+ to Ti3+, offering a theoretical capacity of about 240 mAh/g depending on the atomic weight of M (Table 1). The mechanism of lithium insertion is unclear, and only about 75% of theoretical capacity has been attained.

#### Table 1. Space Group, Charge Capacity, and Li Uptake per Formula Unit of the MLi2Ti6O14 Titanates

<table>
<thead>
<tr>
<th>anode material</th>
<th>space group</th>
<th>charge capacity (mAh/g)</th>
<th>operating voltage (V) vs Li</th>
<th>Li uptake (per f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na4Li2Ti6O14</td>
<td>Cmca</td>
<td>62</td>
<td>1.28</td>
<td>1.32</td>
</tr>
<tr>
<td>SrLi2Ti6O14</td>
<td>Cmca</td>
<td>111</td>
<td>1.42</td>
<td>2.74</td>
</tr>
<tr>
<td>BaLi2Ti6O14</td>
<td>Cmca</td>
<td>125</td>
<td>1.38</td>
<td>2.85</td>
</tr>
<tr>
<td>PbLi2Ti6O14</td>
<td>Cmca</td>
<td>162</td>
<td>1.35</td>
<td>4.40</td>
</tr>
</tbody>
</table>

Na4Li2Ti6O14 is the lightest among MLi2Ti6O14 (M = 2Na, Sr, Ba, and Pb) and so it is expected to have the highest theoretical capacity of 282 mAh/g for six Ti redox (Figure 1i). However, due to the geometrical constraints, it cannot insert more than two Li (62 mAh/g, 1.3 Li) as the vacant 11 coordinated interlayer sites are fully filled with two monovalent Na atoms, compared to the half-filled interlayer by one divalent M atom (M = Sr, Ba, and Pb) in the remaining members (enabling them to incorporate up to 4.4 Li) (Figure 1j–m). Furthermore, even the divalent counterparts with half-filled interlayers are space limited as they reversibly allow only four lithium ions (instead of six) via reduction of four out of six Ti ions. Lithium ions (de)insert from 1.2 to 1.5 V in the system, with each member showing its signature (de)insertion voltage (Figure 1n–q). The observed charge capacity is in the order BaLi2Ti6O14 (111 mAh/g, 2.7 Li) < SrLi2Ti6O14 (125 mAh/g, 2.9 Li) < PbLi2Ti6O14 (162 mAh/g, 4.4 Li). While a slightly higher observable capacity in the Sr analog compared to Ba is in line with the trend in their theoretical capacity, the reason why PbLi2Ti6O14 shows the largest capacity and uptakes significantly more lithium despite being the heaviest is highly intriguing. To address this question, we embark on investigating the thermodynamic stability in this family of compounds.

#### Thermodynamic Studies.

Thermochromicaric data are sensitive to the crystal structure, phase, and chemical purity of the sample. PXRD and TG-DSC measurements were performed before the calorimetric measurement to detect any possible contamination/decomposition and check for adsorbed
water on the sample due to exposure in the ambient atmosphere prior to calorimetric experiments. Samples were phase pure as shown in Figure 1a–d, and TGA measurements detected no mass loss, confirming there was no adsorbed water on the samples.

The drop solution enthalpy ($\Delta H_{ds}$) and formation enthalpy from oxides ($\Delta H^\circ_{f,ox}$) of MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) as a function of Li uptake per unit formula are shown in Table 2 and Figure 2a,b. The enthalpy of drop solution of PbO, SrO, and BaO is obtained from the drop solution enthalpy of lead oxide and strontium and barium carbonate (PbO, SrO, and BaO) as a function of Li uptake per unit formula are shown in Table 2 and Figure 2a,b. The enthalpy of drop solution of MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) Titanates (a) Dissolution enthalpy (b) formation enthalpy vs reversible Li uptake (per formula unit) in the lithium titanates, and (c) enthalpies of formation from oxides for lithium titanates as a function of acidity based on Smith’s scale of acidity for alkali, alkali-earth, and lead oxides.

Table 2. Drop Solution Enthalpies ($\Delta H_{ds}$) in 3Na$_2$O·4MoO$_3$ at 800 °C and Formation Enthalpies ($\Delta H^\circ_{f,ox}$) at 25 °C of MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) Titanates

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H_{ds}$ (kJ/mol)</th>
<th>$\Delta H^\circ_{f,ox}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$Li$_2$Ti$<em>6$O$</em>{14}$</td>
<td>502.41 ± 0.35(8)</td>
<td>-333.32 ± 4.91</td>
</tr>
<tr>
<td>BaLi$_2$Ti$<em>6$O$</em>{14}$</td>
<td>506.75 ± 0.57(8)</td>
<td>-323.54 ± 3.44</td>
</tr>
<tr>
<td>SrLi$_2$Ti$<em>6$O$</em>{14}$</td>
<td>498.16 ± 0.68(8)</td>
<td>-260.65 ± 3.15</td>
</tr>
<tr>
<td>PbLi$_2$Ti$<em>6$O$</em>{14}$</td>
<td>508.46 ± 0.46(8)</td>
<td>-157.81 ± 2.54</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>-77.21 ± 2.44</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-195.90 ± 4.23</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>73.70 ± 0.39(6)</td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td>-127.48 ± 1.84</td>
<td></td>
</tr>
<tr>
<td>BaO</td>
<td>-181.22 ± 2.32</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>-14.34 ± 0.38(6)</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>37.40</td>
<td></td>
</tr>
</tbody>
</table>

This work. The value is the mean of the number of experiments indicated in parentheses; two standard deviations are given as errors.

PbO, SrO, and BaO is obtained from the drop solution enthalpy of lead oxide and strontium and barium carbonate (SrCO$_3$ and BaCO$_3$) at 800 °C using the thermochemical cycle in Tables S5 and S6 (Supporting Information). The enthalpies of drop solution of Li$_2$O, Na$_2$O, and TiO$_2$ are taken from our previous measurements. $\Delta H^\circ_{f,ox}$ of MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) is calculated from the thermochemical cycles in Table 3.

The $\Delta H_{ds}$ for lithium titanates is endothermic ranging from 498.16 ± 0.68 to 508.46 ± 0.46 kJ/mol, and $\Delta H^\circ_{f,ox}$ is exothermic ranging from −333.32 ± 4.91 to −157.81 ± 2.54 kJ/mol, confirming that the these materials are thermodynamically stable. $\Delta H_{ds}$ does not follow any regular trend but $\Delta H^\circ_{f,ox}$ is inversely proportional to lithium uptake in MLi$_2$Ti$_6$O$_{14}$ (Figure 2b). The least stable PbLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = -157.81 ± 2.54$ kJ/mol) intercalates the most lithium (4.4 Li), followed by SrLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = -260.65 ± 3.15$ kJ/mol, 3.08 Li), then BaLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = -323.54 ± 3.44$ kJ/mol, 2.47 Li), while the most stable NaLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = -333.32 ± 4.91$ kJ/mol) inserts the least lithium (1.32 Li).

Factors such as size of the metal ion, geometrical and compressive strains, and “acid–base” interaction explains their stability trend.

The energetics of ternary oxide formation is dominated by the difference in the acid–base character of the cations. Binary oxides are classified as acidic, basic, or amphoteric. Smith’s table$^{25}$ expresses all metal oxides in terms of acidity and the enthalpies of formation from binary oxides for lithium titanates change linearly with acidity. This validates the trends observed in the formation enthalpies, and in turn the lithium uptake (Figure 2c). The highly exothermic heats of formation reflect strong acid–base interactions among the MO, and Li$_2$O (basic oxides) with TiO$_2$ (a somewhat acidic oxide). The basic binary oxides MO and Li$_2$O interact with the acidic TiO$_2$ to form the MLi$_2$Ti$_6$O$_{14}$ structure. Alkali metal oxides exhibit greater basic character followed by alkaline earth metal oxides, among the divalent oxides those of larger cations are more basic compared to lighter cations, the order of basicity for MO is Na$_2$O > BaO > SrO. $^{31}$ Thus, the acid–base interaction between MO, Li$_2$O, and TiO$_2$ which stabilizes the structure most strongly in Na$_2$Li$_2$Ti$_6$O$_{14}$, followed by BaLi$_2$Ti$_6$O$_{14}$ then SrLi$_2$Ti$_6$O$_{14}$. This explains the trend observed in the $\Delta H^\circ_{f,ox}$ Na$_2$Li$_2$Ti$_6$O$_{14}$ > BaLi$_2$Ti$_6$O$_{14}$ > SrLi$_2$Ti$_6$O$_{14}$. This correlation is consistent with the dominance of the acid–base chemistry in phase stability, as seen in trends of enthalpies of formation in
Table 3. Thermodynamic Cycles Used to Calculate Formation Enthalpies (ΔH°f,ox) of MLi₂Ti₆O₁₄ at 25 °C

<table>
<thead>
<tr>
<th>reaction</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLi₂Ti₆O₁₄ (s,25°C) → MO (s,25°C) + Li₂O (s,25°C) + 6TiO₂ (s,25°C)</td>
<td>ΔH₁ = ΔH₂ (MLi₂Ti₆O₁₄)</td>
</tr>
<tr>
<td>Li₂O (s,25°C) → Li₂O (s,25°C)</td>
<td>ΔH₁ = 77.21 ± 2.44⁷⁵</td>
</tr>
<tr>
<td>Na₂O (s,25°C) → Na₂O (s,25°C)</td>
<td>ΔH₁ = 195.90 ± 4.23⁷⁷</td>
</tr>
<tr>
<td>TiO₂ (s,25°C) → TiO₂ (s,25°C)</td>
<td>ΔH₁ = 73.70 ± 0.39⁷⁶</td>
</tr>
<tr>
<td>SrO (s,25°C) → SrO (s,25°C)</td>
<td>ΔH₁ = 127.48 ± 1.84⁷⁸</td>
</tr>
<tr>
<td>BaO (s,25°C) → BaO (s,25°C)</td>
<td>ΔH₁ = 181.22 ± 2.32⁷⁹</td>
</tr>
<tr>
<td>PbO (s,25°C) → PbO (s,25°C)</td>
<td>ΔH₁ = 14.34 ± 0.38⁷⁹</td>
</tr>
<tr>
<td>MO (s,25°C) + Li₂O (s,25°C) + 6TiO₂ (s,25°C) → MLi₂Ti₆O₁₄ (s,25°C)</td>
<td>ΔH₁ = ΔH₂ (MLi₂Ti₆O₁₄)</td>
</tr>
</tbody>
</table>

This work.

many other compounds, including perovskites, olivines, tungstates, carbonates, nitrides and oxynitrides, and glasses.29,30,32–36

The enthalpy of formation from oxides is additionally influenced by the space constraints. In Na₂Li₂Ti₆O₁₄, monovalent sodium occupies the 11-fold site completely as opposed to the divalent counterparts which occupy only half of it. Thus, for the sodium compound, there is no vacant site available for further lithium insertion in the structure. However, in MLi₂Ti₆O₁₄ (M = Sr, Ba, and Pb), despite having similar, additional vacant sites, the divalent members uptake lithium differently. This could be due to size of the metal ions, acid–base interactions as discussed earlier, and the compressive strain induced by the ion at the 11-fold coordinated site. Low bond valence sum (BVS) for Sr (1.75) and Pb (1.79) indicates no residual strain at these sites whereas in Ba (2.11) due to its high BVS has a shortened Ba–O length which results in a compressive strain, straining the lithium pathway to interstitial sites.

The difference in the Li uptake by MLi₂Ti₆O₁₄ (M = Sr and Pb), regardless of having no compressive strain and similar ionic radii of Sr and Pb, is puzzling. The trend of decreasing stability in the ΔH°f,ox is Na₂Li₂Ti₆O₁₄ > BaLi₂Ti₆O₁₄ > SrLi₂Ti₆O₁₄ > PbLi₂Ti₆O₁₄. The low stability of PbLi₂Ti₆O₁₄ is attributed to the amphoteric nature of PbO. Consequently, the acid–base interaction between PbO, Li₂O, and TiO₂ is weak compared to alkali and alkaline earth metal oxides; thus, there is decline in the stability of PbLi₂Ti₆O₁₄. Similar differences are seen in comparing lead and strontium silicate glasses.37 This is in corroboration to the Smith’s scale of acidity.

Depending on the stability of these lithium titanates, the amount of Li uptake varies during charge cycles. The least stable PbLi₂Ti₆O₁₄ gains stability by intercalating 4.4 Li, whereas the slightly more stable SrLi₂Ti₆O₁₄ intercalates only 2.9 Li. The most stable Na₂Li₂Ti₆O₁₄ and Na₂Li₂Ti₆O₁₄ intercalate 2.7 and 1.3 Li. Future calorimetric measurements on samples with intermediate charge cycles having a variable amount of Li in the 11-coordination site for the MLi₂Ti₆O₁₄ (M = Ba, Sr, and Pb) structures would provide more insight into the stability.

CONCLUSIONS

It can be concluded that there is strong correlation between the thermodynamic stability and the lithium uptake in this class of materials. Strong exothermic acid–base reactions between MO, Li₂O, and TiO₂ result in large exothermic enthalpies of formation, indicating that MLi₂Ti₆O₁₄ are thermodynamically stable. Depending on the nature of acid–base interactions, the stability varies, alkali metals exhibit greater basic character followed by alkaline earth metal oxides, and among the alkaline earth metal oxides, those of larger cations are more basic compared to lighter cations, and the order of basicity for MO is Na₂O > BaO > SrO. PbO is an amphoteric oxide for which the acid–base interaction is weak compared to alkali or alkaline earth metal oxides. Thus, the thermodynamic stability diminishes in the order Na₂Li₂Ti₆O₁₄ > BaLi₂Ti₆O₁₄ > SrLi₂Ti₆O₁₄ > PbLi₂Ti₆O₁₄ which is directly proportional to the acid–base interactions. The trends in stability also depend on the charge and size of the cation and the compressive strain which are typical for interoxidic compounds. The formation enthalpy in these materials is inversely proportional to the lithium uptake during charge cycles. Least stable PbLi₂Ti₆O₁₄ uptakes most Li (4.4 Li), and the most stable Na₂Li₂Ti₆O₁₄ uptakes least Li (1.3 Li).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c05701. Rietveld refinement of MLi₂Ti₆O₁₄ (M = Sr, Ba, and 2Na) titanates and thermodynamic cycles used to calculate the drop solution enthalpy (ΔH°s) of SrO and BaO in sodium molybdate at 800 °C (PDF)

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