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On the Synthesis of Ramsdellite $LiTiMO_4$ (M = Ti, V, Cr, Mn, Fe): An Experimental and Computational Study of the Spinel–Ramsdellite Transformation

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The $LiTiMO_4$ (spinel) ↔ $LiTiMO_4$ (ramsdellite) transformation has been investigated by combining computational and experimental techniques, for M = Ti, V, Cr, Mn, and Fe, in order to understand the characteristics of this transformation and the influence of the metal M on the relative stability of the ramsdellite polymorph. The calculations predict that all the aforementioned $LiTiMO_4$ spinels are thermodynamically stable with respect to the ramsdellite polymorph, with the calculated enthalpy variation of the transformation being less than 40 $kJ\,mol^{-1}$. In the case of normal spinels $[Li]_t[TiM]_oO_4$ we estimated a transformation temperature in the range 900–1600 °C, whereas the polymorphic transformation for inverse spinels $[Li_{0.5}M_{0.5}]_t[TiM_{0.5}Li_{0.5}]_oO_4$ is accompanied by a lower entropy gain, hence a much higher temperature would be needed to overcome the enthalpy of the transformation. The transformation is thus entropically controlled. Accordingly, experimental results show that normal $[Li]_t[TiM]_oO_4$ spinels (M = Ti, V, Cr) readily transform into ramsdellites at temperatures between 900 and 1400 °C, whereas this transition is hindered for spinels $LiTiMO_4$ (M = Fe, Mn), which possess a high degree of inversion. Based on a possible mechanism for the transformation, we infer that the impossibility of transforming the Mn and Fe inverse-spinels into their ramsdellite forms is also due to the high energy barriers that must be overcome during the transformation. The obtained $LiTiMO_4$ (M = Ti, V, and Cr) ramsdellites, which contain Ti^{IV} and M^{III}, display a twofold electrochemical application, namely that one lithium ion per formula unit can be inserted into these compounds at about 1.4 V vs. Li (reduction of Ti^{IV} to Ti^{III}). The oxidation of M^{III} ions to M^{IV} enables lithium deinsertion from $LiTiMO_4$ (M = Ti, V, and Cr) at potentials of 1.9 V (M = Ti), 3.1 V (M = V), and 4.2 (M = Cr) vs. Li.

Introduction

Electrode materials for rechargeable lithium batteries are based on transition metal inorganic frameworks that can reversibly intercalate large amounts of lithium ions. The application of such materials as positive or negative electrodes depends on the potential at which lithium ions are intercalated − potentials above 3 V and below 1 V vs. Li are desirable for the positive and the negative electrode, respectively. In terms of lithium battery applications, titanates with the ramsdellite structure are of considerable interest because this structure enables fast and reversible insertion of a good quantity of lithium ions. A schematic representation of the ramsdellite structure is depicted in part a of Figure 1. It is built up by $[TiO]_6$ octahedra that form double edge-sharing chains running along [001]. These chains are interconnected through corners in the *ab* plane. Lithium ions partially occupy some crystallographic sites located in the 1×2 tunnels running parallel to the *c* axis.[1,2] The presence of unoccupied Li sites in these channels in ramsdellite $Li_2Ti_3O_7$ allows for a further lithium uptake of up to 2.24 Li ions, which means that $Li_2Ti_3O_7$ would deliver a specific capacity of 240 $Ah\,kg^{-1}$ as an electrode in a lithium cell.[3] The high temperature polymorph of spinel $LiTi_2O_4$ also presents the ramsdellite structural type. Hereafter the spinel polymorph will be denoted as $LiTi_2O_4$(S) while the ramsdellite polymorph will be denoted as $LiTi_2O_4$(R). The latter has recently been proposed as a new electrode material for lithium batteries.[4–6] $LiTi_2O_4$(R) is nominally formulated as $LiTi^{3+}Ti^{4+}O_4$, therefore lithium intercalation into this material proceeds only up to a maximum of one Li per formula unit (specific capacity of 160 $Ah\,kg^{-1}$), in other words complete reduction of the Ti^{4+} ions. The reversible reduction of Ti^{4+} ions in both $Li_2Ti_3O_7$ and $LiTi_2O_4$ occurs at 1.4 V vs. the lithium electrode.

The presence of Ti^{3+}, which can be oxidised, in $LiTi_2O_4$(R) permits the deintercalation of a maximum of one Li per formula unit. Indeed, the extraction of lithium from

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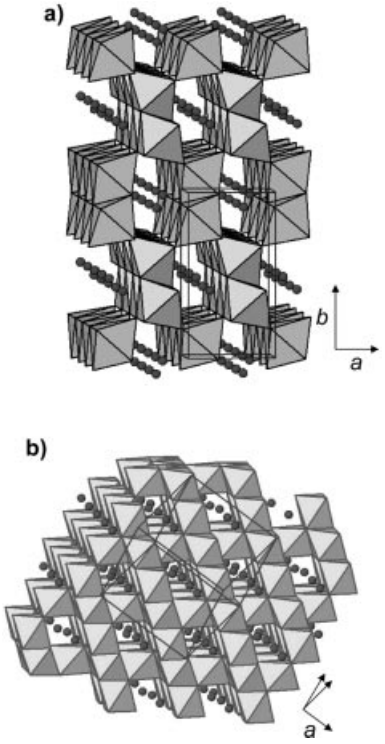

Figure 1. Schematic representation of a) the ramsdellite structure of $Li_2Ti_3O_7$ and b) the spinel structure of $LiTi_2O_4$. In both cases circles correspond to lithium ions and octahedra represent TiO_6 coordination.

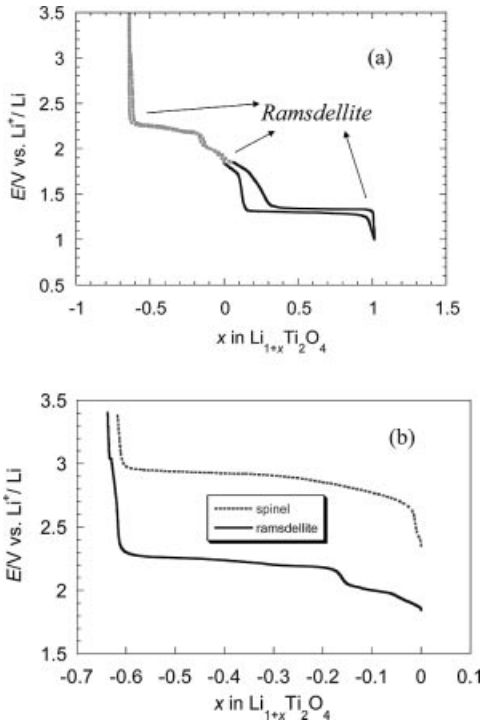

Figure 2. (a) Voltage vs. composition curve of a $LiTi_2O_4$ (ramsdellite)//Li cell started on discharge (continuous line) and started on charge (dashed line). (b) Voltage vs. composition curve of a $LiTi_2O_4$//Li cell started on charge showing the behavior of the two different polymorphs [ramsdellite (continuous line) and spinel (dashed line)].

$LiTi_2O_4$ at room temperature by both chemical and electrochemical methods has been reported as a route to the ramsdellite polymorph of TiO_2.[4,7] Thus, the coexistence of Ti^{3+} and Ti^{4+} in $LiTi_2O_4$ allows for the deinsertion of one lithium ion (oxidation of Ti^{3+}) and the insertion of one lithium ion (reduction of Ti^{4+}). Figure 2 (a) shows a typical voltage composition plot obtained when a Li//$LiTi_2O_4$(R) cell is cycled between either 1.8 and 1 V (continuous line) or 1.8 and 3.5 V (dashed line), which correspond to the intercalation of lithium into $LiTi_2O_4$(R) and de-intercalation of lithium from $LiTi_2O_4$(R), respectively. Both processes are reversible. The flat intercalation and de-intercalation regions are characteristic of two-phase domains, as indicated in previous works[4,5] and confirmed by in situ XRD studies using synchrotron radiation.[8] At the end of the intercalation (1 V) and de-intercalation curves (3.5 V), two different ramsdellites with formulae $Li_2Ti_2O_4$ and TiO_2, respectively, exist. In other words, the intermediate $Li_xTi_2O_4$ composition located at the plateaux actually corresponds to mixtures of the two ramsdellite extremes (x = 0, 1, or 2) in different ratios.

The main advantage of ramsdellites as an electrode material for rechargeable lithium batteries is the high reversibility of the intercalation process. It has been demonstrated that electrochemically inserted $Li_{2+x}Ti_3O_7$ compounds retain the ramsdellite framework for large amounts of lithium ($x \approx 2.24$). The small changes in the basic ramsdellite cell parameters during the intercalation process, also known as zero-strain behavior, are likely to be the origin of the good capacity retention with cycling.[3] The formation of $Li_2Ti_2O_4$(R)/TiO_2(R) upon reduction/oxidation of $LiTi_2O_4$ is also accompanied by very small volume changes. Bearing in mind the good reversibility and high capacity of ramsdellites, we have been working on the synthesis and characterization of novel $LiTi_{2-y}M_yO_4$ ramsdellites obtained by substitution of the trivalent Ti by other ions. The oxidation of Ti^{3+} in $LiTi_2O_4$ occurs at about 1.9 V and it is therefore desirable to increase this potential to the 3–4 V range, as the V^{3+}/V^{4+}, Fe^{3+}/Fe^{4+}, Mn^{3+}/Mn^{4+}, and Cr^{3+}/Cr^{4+} redox couples are known to be operative at such high voltages vs. Li.

Although $LiTi_2O_4$ can be prepared in the ramsdellite structure, its stable form at room temperature is spinel-like. Transformation of $LiTi_2O_4$(S) into $LiTi_2O_4$(R) occurs at 925 °C.[9,10] On the other hand, spinels with the formula $LiTiMO_4$ (M = Ti, V, Cr, Mn, and Fe) are known to exist. With the aim of preparing the novel ramsdellites $LiTiMO_4$ (M = V, Cr, Mn, and Fe), in this work we will try to induce the spinel–ramsdellite phase transformation by thermal treatment in a reaction that can be written as:

$$LiTiMO_4(S) \leftrightarrow LiTiMO_4(R) \quad (1)$$

The relative thermodynamic stability of polymorphs can be explored by first-principles methods, a good example of which is the investigation of Reed et al.[11] dealing with the stability of layered $Li_{0.5}MO_2$ with respect to its transformation into spinel LiM_2O_4 (M is a transition metal). In this

work we have performed a computational study on the stability of ramsdellite with respect to the spinel form to assess whether the transformation of spinel $LiTiMO_4$ (M = V, Cr, Mn and Fe) to ramsdellite is feasible from a thermodynamic point of view. Based on these predictions we have attempted to synthesize the new ramsdellites $LiTiMO_4$ (M = V, Cr, Mn and Fe) starting from the spinel-like polymorphs. A preliminary structural characterization is also presented for those ramsdellites that have been obtained. Finally, although full electrochemical studies of individual ramsdellites are described elsewhere,[12–14] the general electrochemical behavior of the novel ramsdellites is also included here for completeness.

Results and Discussion

Computational Analysis of the $LiTiMO_4$(S) ↔ $LiTiMO_4$(R) Transformation

Computing the energy of a periodic electronic structure requires a cation-ordering scheme to be imposed on the simulated unit cell. The unit cell of $LiTiMO_4$(S) contains eight formula units and shows cubic symmetry (space group *Fd3m*) with a lattice parameter *a* of about 8.2 Å. In this cell we have imposed the simplest order in which Ti and M atoms alternate in the octahedral sites of the spinel along two main crystallographic directions. By doing so, the *Fd3m* symmetry is broken and the new cell must be redefined in the *Imma* space group. The lattice parameters of the ordered structure are $a = a_o/\sqrt{2}$, $b = a_o/\sqrt{2}$, and $c = a_o$, where a_o denotes the lattice parameter of the cubic spinel ($a_o \approx 8.2$ Å). Hence, the unit cell of the ordered spinel (space group *Imma*) is related to that of the cubic spinel (space group *Fd3m*) by a 45° rotation around the *c* axis. In the case of the ramsdellite compounds, M and Ti ions alternate along the [010] direction in the ordered cell used for the calculations in such a way that chains of either M or Ti edge-sharing octahedra run parallel to the [001] axis.

Tables 1 and 2 list the optimized values of the lattice parameters for spinel and ramsdellite $LiTiMO_4$ (M = Ti, V, Cr, Mn and Fe) obtained in this ab initio study. It should be noted that all the transition metal ions occupy octahedral sites in the computed spinel cell. However, experimental results indicate that in the case of M = Cr, Mn and Fe some transition metal ions are located in the tetrahedral sites.[15–18] Note that in the first part of this computational study we have not considered the degree of inversion. In view of the data in Tables 1 and 2, it can be concluded that, generally speaking, the calculation method allows a correct prediction of the cell parameters, with differences of around 2–4% that are typical for state-of-the-art approximations to density functional theory in transition metal oxides. It is well documented that the generalized gradient approximation (GGA) method has a tendency to overestimate the equilibrium volume.

Table 1. Calculated and experimental lattice parameters of spinels $LiTiMO_4$ (M = Ti, V, Cr, Mn, and Fe). The parameters are given for a cell of *Imma* symmetry (four $LiTiMO_4$ formula units per cell) that was used for the calculations (see text). Experimental data are given in parentheses.

	a [Å]	*b* [Å]	*c* [Å]	*V* [Å^3]	Err[a] [%]	Ref.
$LiTi_2O_4$	5.967	5.967	8.439	300.50		
	(5.9430)	(5.9430)	(8.405)	(296.85)	1.23	[10]
$LiTiVO_4$	5.978	5.846	8.416	294.12		
	(5.8237)	(5.8237)	(8.236)	(279.33)	5.29	[19]
$LiTiCrO_4$	5.933	5.948	8.333	294.07		
	(5.867)	(5.867)	(8.297)	(285.58)	2.97	[19]
	(5.882)	(5.882)	(8.318)	(287.76)	2.19	[20]
	(5.875)	(5.875)	(8.308)	(286.72)	2.56	[21]
$LiTiMnO_4$	6.013	6.072	8.208	299.68		
	(5.919)	(5.919)	(8.371)	(293.29)	2.17	[16]
	(5.893)	(5.893)	(8.334)	(289.42)	3.55	[18]
$LiTiFeO_4$	5.981	5.981	8.448	302.20		
	(5.910)	(5.910)	(8.358)	(291.93)	3.52	[22]
	(5.913)	(5.913)	(8.362)	(292.36)	3.36	[17]

[a] Error between calculated and experimental data.

In the last year first-principles calculations have been widely use to accurately predict the lithium intercalation voltage of a large variety of electrode materials (see, for instance, refs.[23–25]). The average lithium de-intercalation voltages of $LiTi_2O_4$ for both ramsdellite and spinel structural types have also been computed in this work as some of them are known experimentally and their comparison may be a convenient way of validating the calculations. Since the insertion reaction is written as Equation (2) the open-circuit average voltage for the lithium insertion pro-

Table 2. Calculated and experimental lattice parameters of ramsdellites $LiTiMO_4$ (M = Ti, V, Cr, Mn and Fe) with two $LiTiMO_4$ formula units per cell. Experimental data are given in parentheses.

Compound	*a* [Å]	*b* [Å]	*c* [Å]	*V* [Å^3]	Err[a] [%]	Ref.
$LiTi_2O_4$	5.071	9.745	2.961	146.319		
	(5.0342)	(9.6201)	(2.9481)	(142.781)	2.48	[10]
$LiTiVO_4$	5.043	9.649	2.962	144.16		
	(5.0090)	(9.5570)	(2.9424)	(140.857)	2.34	this work
$LiTiCrO_4$	4.978	9.597	2.952	141.03		
	(4.9818)	(9.503)	(2.9263)	(138.541)	1.79	this work
$LiTiMnO_4$	5.051	9.876	2.949	147.10	–	this work
$LiTiFeO_4$	5.074	9.807	2.995	149.04	–	this work

[a] Error between calculated and experimental data.

cess can be obtained as explained by Aydinol et al.[24] from a total energy difference expression [see Equation (3); E_{total} refers to the total energy per formula unit] if entropy and volumetric effects are ignored.

$$Ti_2O_4 + Li \leftrightarrow LiTi_2O_4 \quad (2)$$

$$V_a = E_{total(Ti_2O_4)} + E_{total(Li)} - E_{total(LiTi_2O_4)} \quad (3)$$

Calculations predict an average lithium insertion voltage of 1.86 V for TiO_2(R), which is about 0.3 V below the experimental results presented in Figure 2 (b). Such voltage underestimations are usually reported in the literature for transition metal oxides in the GGA implementation (see, for instance, refs.[24,26]). Regarding the spinel, the calculated potential is 3 V, which is in good agreement with the experimental data (see Figure 2, b).

The relative thermodynamic stability of both spinel and ramsdellite $LiMTiO_4$ can be inferred from the difference between their calculated total energies. The results obtained for M = Ti, V, Cr, Mn, and Fe are summarized in Figure 3 for normal (squares) and inverse spinels (circles). The spinel structure is energetically more stable than the ramsdellite form in all cases. To produce a phase transformation between the polymorphs the free-energy variation of Equation (1) should be zero:

$$\Delta G_r = \Delta E_r + P\Delta V_r - T\Delta S_r \quad (4)$$

In this equation E_r is the reaction energy, whose calculated values are given in Figure 3, and the term $P\Delta V_r$ can be obtained from the calculated volume data summarized in Tables 1 and 2. At ambient pressure the $P\Delta V_r$ term has a small value of the order of 10^{-4} kJ mol^{-1}, and is therefore negligible compared to the energy of the reaction (E_r is of the order of 10^1 kJ mol^{-1}). Obviously, the transformation is an endothermic reaction ($\Delta H_r = \Delta E_r + P\Delta V_r$, $\Delta H_r \approx \Delta E_r$). Even if the polymorphic transformation has a positive reaction enthalpy, it might occur if a large positive entropy accompanies the transformation reaction. In this case, the transformation would become favorable at high temperature ($\Delta H_r = T\Delta S_r$). This is indeed found experimentally in the case of M = Ti, since it is well known that the spinel is the low-temperature polymorph and that the transformation to ramsdellite requires heating at 925 °C and final quenching to room temperature. Computational results indicate that the enthalpy of transformation between spinel and ramsdellite $LiTi_2O_4$ is about 24.14 kJ mol^{-1}. The free-energy difference between polymorphs at the transition temperature is zero, therefore the enthalpy variation of the reaction is equal to the $T\Delta S_r$ term. First-principles investigations do not provide information about the entropy term, which makes it impossible to predict the transition temperature. However, the entropy term can be approximated for the $LiTi_2O_4$(S)–$LiTi_2O_4$(R) transformation, which occurs at a temperature of 925 °C. Thus, taking into account the calculated value of the enthalpy (24.14 kJ mol^{-1}), the entropy value for this transformation is 20.13 J mol^{-1} K^{-1}. To estimate the temperature needed for the remaining $LiMTiO_4$ spinels we can assume that the entropy variation between the normal spinel and the ramsdellite forms is similar for any M.

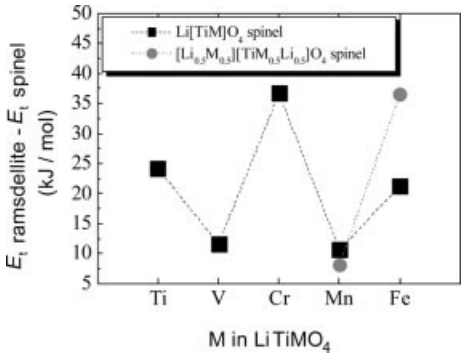

Figure 3. Calculated total energy difference between the ramsdellite and spinel polymorphs for $LiTiMO_4$ (M = Ti, V, Cr, Mn, and Fe). Two configurations, namely the normal cationic distribution $[Li]_t[TiM]_oO_4$ (squares) and the inverse $[Li_{0.5}M_{0.5}]_t[TiM_{0.5}Li_{0.5}]_oO_4$ configuration (circles), were computed for the spinel structure.

The energy difference between the Fe-substituted ramsdellite and the normal spinel (21 kJ mol^{-1}) is close to that of the $LiTi_2O_4$ system, therefore calculations suggest that $LiTiFeO_4$(R) could be stabilized by similar thermal treatment (considering ΔS to be 0.02 kJ mol^{-1} K^{-1}). In light of this entropy value, the phase transformation for M = V and Mn would occur at lower temperatures, at around 300 °C. The spinel-ramsdellite transformation in the Cr system seems to be the most unfavorable since it presents the largest energy difference (36.6 kJ mol^{-1}). This suggests that the transformation would occur at higher temperatures, around 1550 °C.

So far we have discussed the results considering the normal spinel structure $Li_2(Ti_2M_2)_oO_8$, where all the M ions occupy octahedral sites. However, neutron diffraction measurements have shown that Li and Ti ions show a partial inverted distribution in $LiMnTiO_4$ over the tetrahedral and octahedral sites, although a more recent study has suggested that the Mn ion is disordered between these sites.[18] The same situation occurs in $LiFeTiO_4$ with Li and Fe ions.[17,22] The corresponding formulae – $[Li_{0.66}Ti_{0.34}]_{8a}[Li_{0.34}MnTi_{0.66}]_{16d}O_4$ and $[Li_{0.47}Fe_{0.53}]_{8a}[Li_{0.53}Fe_{0.47}Ti]_{16d}O_4$ – suggest inversion degrees of 34% and 53%, respectively. To account for this degree of inversion, in a second stage we have computed the total energy of the spinels $[Li_{0.5}M_{0.5}]_t[Ti_1M_{0.5}Li_{0.5}]_oO_4$ (M = Fe and Mn). In the case of Fe the inverse spinel is 15.8 kJ mol^{-1} more stable than the normal spinel, hence the energy difference between ramsdellite and spinel forms increases by the same amount to 36.5 kJ mol^{-1}, which is the same energy difference found in the Cr system (see Figure 3). The enthalpic stabilization of the inverse spinel with respect to the normal configuration is rooted in the tetrahedral-site preference of Fe^{3+} (although small). In addition, the configurational entropy also

minimizes the free energy of the inverse spinel with respect to the normal spinel. Navrotsky et al.,[27] amongst others, have reported that the configurational entropy in spinels depends on the degree of inversion, and is 11.3 and 14.6 $J\,mol^{-1}\,K^{-1}$ larger for the inverse spinels $B(AB)O_4$ and $A_{0.5}B_{0.5}(A_{0.5}B_{1.5})O_4$, respectively, than for the normal spinel $A(B_2)O_4$. Hence, the inverse spinel↔ramsdellite transformation is accompanied by a lower entropy gain than the normal spinel↔ramsdellite transformation. The entropy of the inverse-spinel↔ramsdellite transformation can be roughly approximated as follows:

$LiTiMO_4$ (normal spinel) ↔ $LiTiMO_4$ (ramsdellite)
$\Delta S \approx 0.02\ kJ\,mol^{-1}\,K^{-1}$

$LiTiMO_4$ (normal spinel) ↔ $[Li_{0.5}M_{0.5}]_t[TiM_{0.5}Li_{0.5}]_oO_4$ (inverse spinel)
$\Delta S \approx 0.015\ kJ\,mol^{-1}\,K^{-1}$[27]

$[Li_{0.5}M_{0.5}]_t[TiM_{0.5}Li_{0.5}]_oO_4$ (inverse spinel) ↔ $LiTiMO_4$ (ramsdellite)
$\Delta S \approx 0.005\ kJ\,mol^{-1}\,K^{-1}$

The estimated entropy variation of the inverse spinel–ramsdellite transformation is 0.005 $kJ\,mol^{-1}\,K^{-1}$, while the calculated enthalpy for the Fe system is 36.5 $kJ\,mol^{-1}$ (Figure 3). With these data, the transformation would occur at about 7000 °C, which is significantly higher than the value of 900 °C estimated for the normal spinel–ramsdellite transformation. These results therefore suggest that the spinel↔ramsdellite transformation is entropically controlled.

The Mn inverse spinel is calculated to be 3 $kJ\,mol^{-1}$ *less* stable than its normal configuration. This apparent disagreement with experiment does not come as a surprise, however, as Mn^{3+} has a large octahedral-site preference and the inverse Mn^{3+} spinels are not enthalpically stabilized. Considering entropic factors, the disorder of cations in the octahedral/tetrahedral sites in the inverse spinels supposes a gain of mixing entropy which, together with the gain of configurational entropy mentioned above, allows to overcome the small energy of 3 $kJ\,mol^{-1}$ at high temperature (DFT refers to zero Kelvin). Therefore the inability of DFT to accurately predict the inversion in Mn spinels is likely rooted in the fact that these spinels are stabilized by entropic factors (configurational and mixing entropy), which cannot be taken into account by first-principles methods. Furthermore, the possibility of valence changes when Mn^{3+} migrates to tetrahedral sites[11,28] also complicates the picture. Concerning the temperature of the $[Li_{0.5}Mn_{0.5}]_t$-$[TiMn_{0.5}Li_{0.5}]_oO_4$ inverse spinel↔ramsdellite transformation, the estimated entropy of 0.005 $kJ\,mol^{-1}\,K^{-1}$ suggests that a temperature of 1327 °C will be needed to produce such a transformation.

As this works aims to prepare novel ramsdellites $LiM^{III}Ti^{IV}O_4$, it is important to determine the oxidation state of M and Ti in the fully relaxed structures of the calculated $LiTiMO_4$ ramsdellites. An approximate oxidation state for Ti and M in the studied compounds can be obtained by integrating the net electron spin density over a radius sphere around each transition metal ion.[11,29] Some of the results are shown in Figure 4 for $LiTi_2O_4$(R) and the substituted ramsdellites with Cr and Mn. The net spin density increases steeply when integrated through the *d*-states of the metal ion up to 1 Å, then a plateau is observed because the charge density of the oxygen ions does not contribute to the spin density. The net spin around Ti ions in $LiTi_2O_4$(R) suggests that the oxidation state of both titanium ions is +3.5, in agreement with the metallic behavior reported previously.[7,30] On the contrary, titanium is present in the substituted ramsdellites $LiTiCrO_4$ and $LiTiMnO_4$ as a diamagnetic tetravalent ion (Ti^{4+}), while both Cr and Mn are in the trivalent state, with three (t_{2g}^3) and four ($t_{2g}^3\ e_g^1$) unpaired electrons, respectively. Similar results are obtained for the $LiTiVO_4$ and $LiTiFeO_4$ spinels.

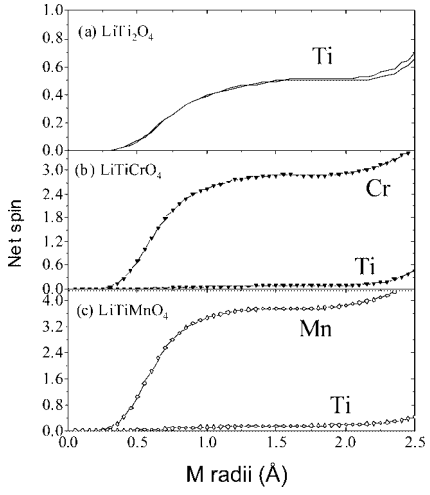

Figure 4. Integral of the net spin density for the calculated $LiTiMO_4$ ramsdellites with M = Ti (a), Cr (b), and Mn (c).

Experimental Study of the $LiTiMO_4$(S) ↔ $LiTiMO_4$(R) Transformation

The computational data suggest that the normal spinel↔ramsdellite transformation could be achieved at temperatures below 1600 °C, whereas the inverse spinel↔ramsdellite transformation is entropically hindered. We therefore attempted to induce the spinel↔ramsdellite transformation for the $LiTiMO_4$ spinels (M = V, Cr, Mn and Fe) as described in the Methodology section. For comparison purposes we also carried out the transformation of $LiTi_2O_4$.

Transformation of $LiTi_2O_4$ was achieved at 950 °C, in agreement with previously reported results.[9,10] A slightly higher temperature (1050 °C) was required for $LiTiVO_4$ since mixtures of spinel and ramsdellite are obtained at lower temperature. The corresponding X-ray diffraction pattern and Rietveld refinement of the new ramsdellite with composition $LiTiVO_4$ are shown in Figure 5 (R_{wp} = 0.062; R_p = 0.048; R_B = 0.088, χ^2 = 1.38). The cell parameters are given in Table 2. The structural model is that corresponding to $LiTi_2O_4$(R) with Ti and V disordered in the octahedral positions. The light lithium ions could not be located from the X-ray data, therefore they were modeled as occupying

the same position as in $LiTi_2O_4$. The lithium parameters were therefore held constant at the start of the refinement, assuming an ideal occupancy of 0.5.

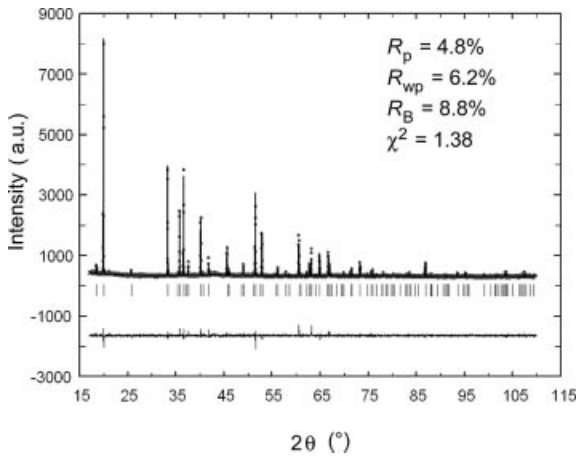

Figure 5. Rietveld refinement plot (experimental, calculated, and difference curve) for ramsdellite $LiTiVO_4$ in the space group *Pbnm* and with a = 5.0090(8), b = 9.5570(1), c = 2.94242(3) Å.

The computational data indicate that the enthalpy of the transformation reaction is lower for V than for Ti. As discussed above, assuming that the entropy change is similar, the transformation temperature should be lower for V than for Ti, which is not what we found experimentally. We note that kinetics may be the origin of this mismatch between estimated and experimental transition temperatures.

The transformation from spinel to ramsdellite for the Cr system occurs over a rather wide temperature range. Transformation begins at around 900 °C but is not complete until about 1250 °C. The evolution of the ratio of each polymorph with temperature was followed by means of high temperature X-ray diffraction. The results are shown in Figure 6. It can be seen that the spinel continuously transforms to ramsdellite following the typical behavior of a two-phase transformation, and a new pure ramsdellite phase is obtained at 1250 °C. The corresponding XRD pattern is similar to that shown in Figure 5 and Rietveld refinement was performed using the same structural model as above (R_{wp} = 0.183; R_p = 0.138; R_B = 0.079, χ^2 = 3.9). The lattice parameters of this new ramsdellite are also given in Table 2. The difference in the temperature needed to obtain $LiTi_2O_4$(R) and $LiTiCrO_4$(R) seems to be related, at least partially, to the larger energy difference calculated between spinel and ramsdellite for $LiTiCrO_4$ in comparison to $LiTi_2O_4$ (see above).

A quite different behavior was found for the Mn and Fe cases. Treatment at temperatures ranging from 925 to 1400 °C produced either no transformation or mixtures of several phases without any evidence of a ramsdellite phase. It therefore seems that the high-temperature polymorph cannot be stabilized for these two cases. This is obviously expected from the computational results, which indicate that the inverse spinel↔ramsdellite transformation is entropically hindered.

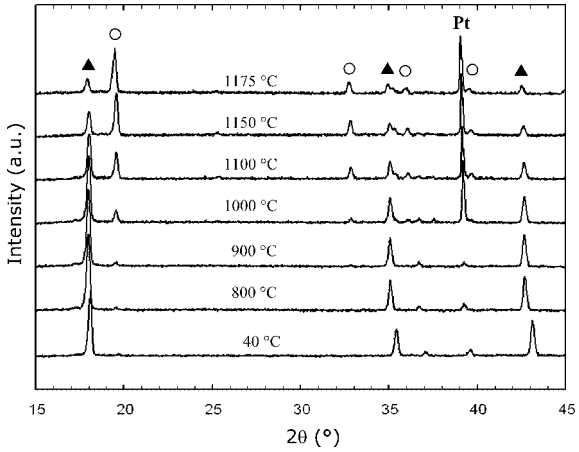

Figure 6. Temperature-resolved in situ X-ray diagrams of the spinel to ramsdellite transition of $LiTiCrO_4$ between 40 and 1175 °C. ▲ spinel reflections, ○ ramsdellite reflections.

We will now consider the possible mechanism for the spinel–ramsdellite transformation. A mechanism for this transformation can be proposed based on the model proposed by Thackeray and co-workers for the process occurring in ramsdellite-like γ-MnO_2.[31,32] A schematic representation is depicted in Figure 7 and can be described in two stages, as follows. The spinel structure initially responds (Figure 7, a) with a cooperative displacement of one quarter of the titanium ions (see arrows on filled octahedra) and half of the lithium ions (see arrows on filled circles). Displacement of the metals is followed by a shear operation of the spinel blocks perpendicular to the (111) spinel direction (dashed arrows in Figure 7, a). A second shear operation in the same direction (dashed arrows in Figure 7, b) produces the hexagonal packed $(Ti_2)O_4$ framework of $LiTi_2O_4$(R) that is shown in Figure 7 (c). It is evident that a relatively high energy is needed to displace the titanium ions from the octahedral sites of the spinel structure to interstitial octahedral sites. The use of high temperatures assists the diffusion of the titanium and lithium cations and rearrangement of the oxygen ions from cubic close packing in the spinel structure to hexagonal packing in the ramsdellite structure. This structural transformation does not, in principle, affect either the tetrahedral coordination of Li or the octahedral coordination of Ti, but it does affect the structural connection between the polyhedra. Thus, while Li ions in the spinel structure are located in the vicinity of titanium ions in vertex-shared octahedra, in the ramsdellite structure the Li ions are located in the vicinity of titanium ions that reside in neighboring face-sharing octahedra. This produces an increase in the electrostatic interaction between face-sharing Li and Ti polyhedra, which means that the phase transformation should be favored for spinels with a normal cationic distribution (the normal spinel structure), whereas an inversion of the cationic distribution, especially of highly charged transition metals in the tetrahedral sites, will destabilize the ramsdellite structure due to electrostatic repulsion

between metal ions in face-sharing polyhedra. Thus, kinetic factors might also hinder the inverse spinel↔ramsdellite transformation.

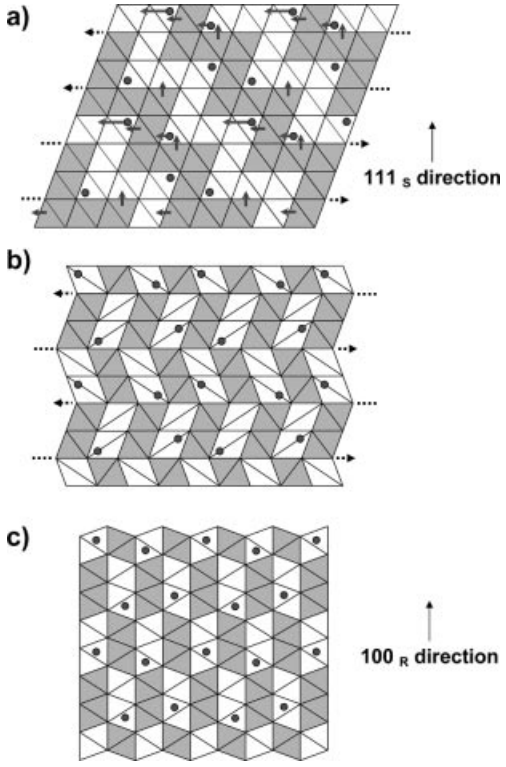

Figure 7. Proposed schematic representation for the spinel $LiTiMO_4$ to ramsdellite $LiTiMO_4$ transformation based on refs.[31,32] Filled octahedra: $(M,Ti)O_6$; small circles: Li^+ ions.

In agreement with this $LiTi_2O_4$(S) and $LiTiVO_4$(S),[19] which are normal spinels, transform readily into the corresponding ramsdellites. $LiTiCrO_4$(S) has been reported by several authors to adopt a normal spinel structure (space group *Fd3m*) with all Li ions at the (tetrahedral) 8a site and a random distribution of Ti and Cr over the (octahedral) 16d site, corresponding to the formulation $[Li]_t[Ti,Cr]_oO_4$,[20,33–36] although a slight inversion (12%) in cationic site distribution regarding Li and Ti has been found by neutron diffraction experiments.[15] This, in addition to the higher enthalpy calculated for the transformation, would account for a more hindered phase transition and mean that the full transformation requires a much higher temperature than in the case of Ti or V. The situation is different for Mn and Fe, however, which present an important degree of inversion, with the proposed cationic distributions being $[Li_{0.66}Ti_{0.34}]_{8a}[Li_{0.34}MnTi_{0.66}]_{16d}O_4$[16,18] and $[Li_{0.47}Fe_{0.53}]_{8a}[Li_{0.53}Fe_{0.47}Ti]_{16d}$.[17,22] We have already discussed that the spinel↔ramsdellite transformation is entropically controlled therefore, in view of the proposed mechanism, the phase transition for the Mn and Fe systems will also be impeded due to enhanced electrostatic repulsions between higher valent cations in neighboring face-sharing polyhedra. The transformation into ramsdellite in these cases must therefore be linked to a more reconstructive mechanism in which all lithium ions would remain in the tetrahedral position and all higher valent transition metals would occupy the octahedral position.

Electrochemistry of the Novel $LiTiVO_4$ and $LiTiCrO_4$ Ramsdellites

The electrochemical behavior of $LiTiVO_4$(R) and $LiTiCrO_4$(R) can be fully interpreted assuming the replacement of Ti^{3+} in $LiTi_2O_4$ by V^{3+} and Cr^{3+}, respectively. Such a hypothesis is in good agreement with the computational results, and has been confirmed by magnetic susceptibility measurements, as reported elsewhere.[13,14,30]

As expected, no significant differences were found for the three ramsdellites $LiTiMO_4$ (M = Ti, V, and Cr) regarding intercalation of lithium (reduction). The same voltage profile is observed down to 1 V, with the plateau characteristic of reduction of Ti^{4+} to Ti^{3+} at about 1.4 V (see part a in Figure 2, continuous line). This result can be explained in terms of the occurrence of the same reaction in all three cases, namely

$$LiTi^{4+}M^{3+}O_4(R) + xLi \rightarrow Li_{1+x}\ Ti^{4+}{}_{1-x}Ti^{3+}{}_x\ M^{3+}{}_xO_4(R);\ x < 1 \quad (5)$$

Figure 8 shows the first charge of a Li//$LiTiMO_4$(R) cell for M = Ti, V, and Cr. Any differences in polarization and quantity of lithium extracted are mainly due to the different electrical conductivity that is expected for the different ramsdellites. The oxidative reaction can be written as

$$LiTi^{4+}M^{3+}O_4(R) \rightarrow Li_{1-x}Ti^{4+}M^{3+}{}_{1-x}M^{4+}{}_xO_4(R) + xLi;\ x < 1 \quad (6)$$

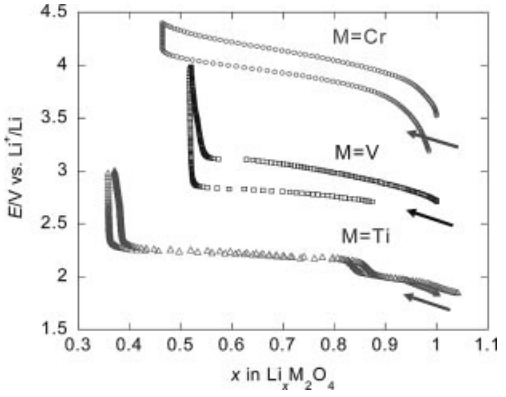

Figure 8. Typical voltage composition plot obtained from galvanostatic experiments (0.1 $mA\,cm^{-2}$) on cells $LiTiMO_4$//Li. Data were recorded by starting the cells first on oxidation followed by reduction down to the initial open circuit voltage.

For M = Ti this process occurs at an average voltage of 1.9 V, as reported previously.[4,5,8] When Ti^{3+} is replaced by V^{3+} the average oxidation voltage increases to 3.1 V, which is characteristic of V^{III} oxidation. The oxidation voltage for $LiTiCrO_4$(R) is shifted to an average voltage of 4.2 V, which is in agreement with the value observed for the Cr^{4+}/Cr^{3+} redox couple in related systems.[37,38] Since the average oxidative voltage of $LiTi_2O_4$ has increased by more than 1 and 2 V for $LiTiVO_4$ and $LiTiCrO_4$, respectively, the electro-

chemical performance of a lithium cell made from either $LiTiVO_4$(R) or $LiTiCrO_4$(R) as the positive electrode is much better. The maximum quantity of lithium that can be de-intercalated is expected to be constant as it is limited by the content of lithium and M^{3+} (one ion per formula unit), therefore the maximum theoretical capacity of $LiTiVO_4$(R) or $LiTiCrO_4$(R) is around 160 $mAh\,g^{-1}$, as in $LiTi_2O_4$. However, the higher oxidation voltage of $LiTiVO_4$ and $LiTiCrO_4$ results in a significant increase of the specific energy delivered by the electrode material of 50% and 100%, respectively.

To sum up the electrochemical performance, it is interesting to note that the new ramsdellites described herein present two different processes at very different voltages that correspond to the oxidation of V^{3+} and Cr^{3+} at high voltage and the reduction of Ti^{4+} at low voltage. The application of these materials in lithium batteries as high voltage cathodes might make use of the former process, while if a low voltage anode material is desired the low voltage process could be used. More detailed studies on performances, mainly regarding cyclability, will be published elsewhere,[13,14] while the influence of the Ti^{3+}/M^{3+} ratio on performance is now under investigation.

Conclusions

As part of our search for novel materials with potential interest as electrodes in lithium batteries, we have reported the preparation of novel $LiTiMO_4$ ramsdellites by inducing a temperature-driven transformation in the corresponding spinel-like forms and have combined computational and experimental techniques to study this $LiTiMO_4$ (spinel) ↔ $LiTiMO_4$ (ramsdellite) transformation.

The computational study performed on the compounds $LiTiMO_4$ (M = Ti, V, Cr, Mn, and Fe) indicates that the spinel form is enthalpically more stable than the corresponding ramsdellite. However, in agreement with the order of the total energy differences (below 40 $kJ\,mol^{-1}$ per formula unit), the spinels can be transformed into their corresponding ramsdellites by thermal treatment. While it is possible to compute the enthalpy of the transformation, it is impossible to predict the temperature at which it will occur. The reasons for these limitations are: (i) first-principle methods refer to zero Kelvin, (ii) calculations are performed for perfectly ordered structures while, experimentally, M and Ti ions randomly occupy the octahedral sites of the ramsdellite/spinel structure. Hence no information about the entropy that accompanies the transformation can be obtained from first principles. The entropy of the transformation has been approximated here from values of temperatures and entropies available in the literature. The estimated temperatures for the $LiTiMO_4$(S) ↔ $LiTiMO_4$(R) transformation are lower than 1600 °C for all the metals studied, hence this transformation is feasible from a thermodynamic point of view. Since the experimental findings showed that the transition metal ions can move to the tetrahedral sites, in a second step we have estimated the temperature of the $LiTiMO_4$(inverse spinel) ↔ $LiTiMO_4$(R) transformation. Our data support that this transformation is entropically hindered.

Experimental results have shown that thermal treatment of spinels $LiTiMO_4$ induces a phase transformation to the ramsdellite-like polymorph for M = Ti, V, and Cr. Indeed, the new ramsdellites $LiTiMO_4$ (M = V and Cr) have been isolated and characterized. Such a transformation could not be detected in the explored temperature range ($T \leq$ 1400 °C) for Fe- and Mn-containing spinels. Therefore the experimental results corroborate that the degree of inversion of the spinel has an influence on the transformation: the transformation only occurs if the starting spinel has a normal cationic distribution while it does not for the inverse spinel. The former situation is found for M = Ti and V, and even for Cr with only a slight degree of inversion, whereas the second situation is found for M = Mn and Fe. We have proposed a mechanism for the transformation in which strong cationic repulsions exist along the transformation pathway in the case of inverse spinels. Thus, in light of the experimental and computational results we can conclude that the impossibility of transforming the Mn and Fe inverse-spinel into their ramsdellite forms is due to at least two reasons, firstly that the transformation is entropically hindered and secondly that there are kinetic limitations due the high energetic barriers that should be overcome during the transformation. At present we cannot say whether the entropy or the kinetic impediment is the main limiting factor of this transformation.

The substituted $LiTiMO_4$ (M = Ti, V and Cr) compounds contain Ti^{4+} and M^{3+}, both of which are ions that are electrochemically active in a lithium cell on reduction (Ti^{4+}/Ti^{3+} couple) or oxidation (M^{3+}/M^{4+} couple). In all the prepared $LiTiMO_4$ ramsdellites the reduction of Ti^{4+} occurs at a similar voltage (1.4 V vs. lithium electrode) and develops the same capacity (160 $Ah\,kg^{-1}$). On the other hand, the measured oxidation potentials of the M^{3+} ions in $LiTiMO_4$ range from around 2 V for $LiTi_2O_4$, to about 3 V for $LiTiVO_4$ and 4 V for $LiTiCrO_4$, with the two latter cases being particularly interesting. The high voltage observed when $LiTiMO_4$(R) (M = V, Cr) are oxidized may allow further development of new high-energy positive-electrode materials for rechargeable lithium batteries.

Taking into account the promising electrochemical performances of $LiTiMO_4$(R), the possible relationship between the transformation of the spinels and the inversion factor may be considered as a guide in the search for new electrode materials for rechargeable lithium batteries based on the ramsdellite structure.

Methodology

Computational

The total energy of $LiTiMO_4$ (M = Ti, V, Cr, Mn and Fe) was calculated using the Vienna ab initio Simulation Package (VASP).[39] The exchange-correlation energy was approximated in the generalized gradient approximation (GGA), using ultra-soft

pseudopotentials. A plane-wave basis set with a kinetic energy cutoff of 500 eV was used. The reciprocal space sampling was done with *k*-point grids of $4\times4\times4$. Relaxation was allowed and the final energies of the optimized geometries were recalculated so as to correct for changes in basis during relaxation. All the calculations are spin-polarized. Calculations were initialized considering a ferromagnetic ordering of ions for normal spinels $Li(TiM)_oO_4$ and ramsdellites. In the case of inverse spinels $[Li_{0.5}M_{0.5}]_t$-$[TiM_{0.5}Li_{0.5}]_oO_4$ antiferromagnetic interactions between ions in the tetrahedral and octahedral sites were considered.

Experimental

The synthesis of ramsdellite $LiTiMO_4$ (M = Ti, V, Cr, Mn, and Fe) was attempted by heating the corresponding spinel-like compounds in the hope of achieving the polymorphic transformation. Different temperatures above 900 °C were used until either full transformation to ramsdellite or decomposition of the corresponding spinel was detected. The spinels were prepared by a ceramic procedure. Thus, in order to minimize loss of lithium oxide, a mixture of Li_2CO_3 and TiO_2 in a 1:1 ratio was fired at 700 °C for 24 h to produce Li_2TiO_3. The carbonate-free product was mixed with stoichiometric amounts of TiO_2 and M_2O_3 (M = Cr, Mn, or Fe) and heated at different temperatures. For M = Ti and V, handling and mixing of the air-sensitive reagents V_2O_3 and Ti_2O_3 was done under argon in a dry glove box (water content < 1 ppm). Mixtures were pressed, wrapped in copper foil, and placed into a quartz ampoule, which was vacuum-sealed and fired. In all cases a typical treatment consisted of heating for 24 h followed by quenching to room temperature.

A preliminary structural characterization was made by means of powder X-ray diffraction with a Bruker D8 high-resolution X-ray powder diffractometer using monochromatic Cu-$K_{\alpha1}$ (λ = 1.5406 Å) radiation produced with a germanium primary monochromator. The diffractometer was equipped with an MBraun PSD-50M position sensitive detector (PSD). For the case of samples containing either trivalent V or Ti the XRD patterns were collected in transmission mode using glass capillaries of 0.5-mm diameter, which were filled inside a glove box. Diffraction patterns were analyzed using the FullProf program.[40] X-ray diffraction experiments at high temperature were performed in the case of $LiTiCrO_4$ with a Siemens D5000 diffractometer working in reflection mode (Cu-$K_{\alpha1}$ radiation) equipped with a Bühler HDKS1 high-temperature chamber. Diffraction patterns at temperatures ranging from 800 to 1200 °C were collected in a selected 2θ range (15–45°).

Electrochemical experiments were performed in Swagelok cells with the following configuration: Li|$LiPF_6$ (1 M) in EC (ethylene carbonate) + DMC (dimethyl carbonate) (2:1) host material + carbon black + binder. Positive electrodes were fabricated as pellets 8 mm in diameter from a mixture consisting of 75–85% (w/w) $LiTiMO_4$ (M = Ti, Cr, V), 20–10% (w/w) carbon black, and 5% (w/w) Kynarflex® (kindly provided by Elf-Atochem). A disk of lithium metal was used as the negative and reference electrode. Commercial Selectipur LP31® (Merck) electrolyte solution for lithium batteries was used. Cells were cycled under galvanostatic conditions at a current density of 0.1 $mA\,cm^{-2}$.

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