Changes in local structure of lithium manganese spinels (Li:Mn = 1:2) characterised by XRD, DSC, TGA, IR, and Raman spectroscopy

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Abstract

A series of LiMn2O4 spinels, obtained by the sol-gel method maintaining constant Li:Mn ratio, were calcined at different temperatures (300–900 °C) to create crystal lattice defects. The structure and electronic properties of the samples were studied by complementary experimental techniques (XRD with Rietveld analysis, BET-N2, DSC, MS-TG/SDTA, electrical conductivity, laser Raman and IR spectroscopy with 2D correlation analysis). The oxygen-spinel equilibrium shifts caused by various calcination in the air and in oxygen free atmosphere modulate the type and concentration of the anionic or cationic defects. The relationship between the local symmetry of MnO6 octahedrons, manifested in symmetric and asymmetric vibrations, seemed to determine the phase transition at around the room temperature. Removing of the degeneration of t2g and eg orbitals, due to Jahn–Teller effect, evolves stabilization energy causing increase of activation energy of electron migration. Distortion of the local symmetry makes impossible the Jahn–Teller effect and in consequence stops the phase transition around room temperature.

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Keywords: LiMn2O4; Structural characterization; Phase transitions; Electrical conductivity; Thermal properties

1. Introduction

Lithium manganese spinel LiMn2O4 is recently one of the most intensively studied cathode materials for 4 V lithium ion batteries, due to its promising electrochemical and economic properties. It may substitute the commercially used LiCoO2, which is toxic and more expensive than LiMn2O4. The latter shows reversible capacity of about 130 mAh/g [1,2]. LiMn2O4 is usually obtained by calcination of mixtures of oxides, carbonates, or hydroxides at high temperatures (700–800 °C) for 24–48 h in air [3,4]. The stoichiometric LiMn2O4 obtained by calcination reveals regular structure in Fd3m space group with the lattice constant (a) of 0.82495(2) nm [5]. It was reported in a previous work that the Li–Mn spinel sample obtained by an alternative sol-gel method and further calcined at 800 °C in air showed the lattice constant equal 0.82517(7) nm [6]. It is thought that the higher value of the lattice constant is related to more homogenous and stoichiometric spinel.

The stoichiometric LiMn2O4 shows a reversible phase transition from cubic to orthorhombic structure around room temperature (~290 K). This transformation is effected by Jahn–Teller distortion of high spin Mn3+ (t2g3 eg1) ions [7,8] with accompanying columnar charge ordering in the manganese sublattice, so called electronic crystallization [9]. Such behaviour is responsible for the decrease of the cell capacity upon cycling [1,10]. It is possible to suppress the phase transition by partial substitution of Mn3+ by 3d metal ions (Cr, Ni, Co, Fe, Cu) [11–15] or Al3+ [16]. In addition, the insertion of lithium excess in octahedral 16d (in place of Mn3+) sites in spinel structure stabilizes that structure [17,18]. Each of the possibilities mentioned above changes the Mn3+/Mn4+ ratio due to the substitution of Mn3+ and/or charge compensation. This is the reason for disappearance of the phase transition, as it appears only if the Mn3+/Mn4+ ratio is within 1–1.18 [16]. Substitution of 3d metal ions into manganese sublattice changes the character of discharge curves [15,19].

In recent work Paolone et al. [20] reported a thermal decomposition of spinel samples during collection of Raman spectra due to laser heating. The authors used very strong radiation (500 kW/cm²) at 632.8 nm, which is near resonance band. They suggested that the correct Raman spectrum of
LiMn$_2$O$_4$ should consist of a broad peak at 580 cm$^{-1}$ with two poorly defined features between 300 and 400 cm$^{-1}$. However, at 625 cm$^{-1}$ Ammenden et al. [21] have found a narrow band that was ascribed to totally symmetric vibration ($A_{1g}$). The same was reported by Julien et al. [22].

In the present work a series of lithium-manganese spinels with constant Li:Mn = 1:2 ratio was prepared by a sol-gel method with subsequent calcination at different temperatures. The obtained samples showed various types of defects and local ordering, which was studied using XRD, IR and Raman spectroscopy in relation to electronic properties. Determined correlation between enthalpy of phase transition and changes in local ordering, which was studied using XRD, IR and Raman spectroscopy in relation to electronic properties. Determined correlation between enthalpy of phase transition and changes in local ordering, which was studied using XRD, IR and Raman spectroscopy in relation to electronic properties. Determined correlation between enthalpy of phase transition and changes in local ordering, which was studied using XRD, IR and Raman spectroscopy in relation to electronic properties.

2. Experimental

A series of lithium–manganese spinels: S300 (Li$_{0.96}$ Mn$_{1.92}$O$_4$), Q600 (Li$_{0.99}$Mn$_{1.96}$O$_4$), Q650 (Li$_{0.983}$Mn$_{1.97}$O$_4$), Q700 (Li$_{0.989}$Mn$_{1.98}$O$_4$), Q800 (LiMn$_2$O$_4$), Q850 (LiMn$_2$O$_3$), and Q900 (LiMn$_2$O$_{3.9}$) was prepared by the sol-gel method [17] using solutions of LiNO$_3$, Mn(CH$_3$COO)$_2$ and concentrated ammonia as the alkalinizing agent. The synthesis was performed under argon flow to prevent uncontrolled oxidation of the Mn$^{2+}$ ions. The obtained xerogel was heated in air up to 300 °C with heating speed equal to 1 °C/min and then decomposed for 48 h at the constant temperature 300 °C. During this process a self-ignition and strong exothermic effect was observed at around 250 °C by SDTA measurements [6]. The residue was ground in agate mortar to provide a brown–black powder. To obtain spinel samples with constant ratio of Li:Mn atomic ratio determined from AAS results was constant and equal to 1.00:1.99. The chemical composition and preparation conditions are shown in Table 1.

The structures of the obtained samples were examined by X-ray powder diffraction method (Saifert XRD 7) using Cu K$_\alpha$ radiation ($\lambda$ = 0.154178 nm) and a graphite monochromator. The diffraction data were collected between 12$^\circ$ and 78$^\circ$ 2$\theta$ angle. The in situ XRD measurements were recorded during heating with Philips X = Pert using Cu K$_\alpha$ radiation. During measurements, the temperature of the sample was controlled by the K-type thermocouple calibrated by the producer. The XRD patterns were analyzed using FULLPROF package [23] based on the Rietveld method and JCPDS (35–782 LiMn$_2$O$_4$) standards. Only a scale factor and lattice parameters were refined. The obtained values of the $R_g$ and $R_p$ factors were equal at least to 3.42 and 8.51%, respectively.

Measurements of surface area were performed in Micro-metrics ASAP 2010 using BET isotherm method. About 500 mg of each sample was preliminary degassed at 200–250 °C under pressure 0.26–0.4 Pa for 2 h. Then, N$_2$ sorption was performed at pressure of 8×10$^{-3}$ Pa.

DSC experiments were performed in Mettler-Toledo 821 calorimeter equipped with an intracooler Haake in 40 μl aluminium crucibles under flow of argon (80 ml/min) within temperature range of −40 to +60 °C. The MS-TGA/SDTA experiments were performed in Mettler-Toledo 851 microthermobalance in 150 μl platinum crucibles under flow of air or argon (60 ml/min) within temperature range of 30–1200 °C. The gas evolved during reaction was analysed by on-line joined quadruple mass spectrometer (Balzers).

Electrical conductivity was measured using a 4-probe method within the range of −40 to +35 °C. To improve the electrical contact between sample and electrodes a silver paste with acrylic resin was used.

Thin pellets containing 10 mg of the lithium–manganese spinel oxide and 200 mg of KBr were used for Raman measurement to prevent any decomposition of the samples. The spectra were recorded at room temperature using a triple grating spectrometer (Jobin Yvon, T 64000). A liquid nitrogen cooled CCD detector (Jobin Yvon, Model CCD3000) was used in these measurements. The spectral resolution of 2 cm$^{-1}$ was set. An excitation wavelength at 514.5 nm was provided by an Ar-ion laser (Spectra-Physics, Model 2025), and the laser power at the sample position was about 20 mW (32 W/cm²) to prevent any decomposition of the samples. Raman scattered light was collected with a 135$^\circ$ geometry, and 5000 scans were accumulated to ensure an acceptable signal-to-noise ratio.

IR measurements were performed for thin pellets that were prepared from the KBr disks used in Raman measurements and containing 2 mg of each lithium–manganese spinel and 200 mg of KBr. The spectra were recorded at room temperature as average of 30 scans using a Brucker infrared spectrometer model EQUINOX 55 equipped with a Nernst rod as the excitation source and DT-GS detector with the spectral resolution of 4 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formula</th>
<th>Average oxidation state of Mn ions</th>
<th>Lattice parameter [nm]</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>S300</td>
<td>Li$<em>{0.96}$Mn$</em>{1.92}$O$_4$</td>
<td>+ 3.66</td>
<td>$a$ = 0.8173(2)</td>
<td>Sol-gel, calcination in air 300 °C/48 h</td>
</tr>
<tr>
<td>Q600</td>
<td>Li$<em>{0.99}$Mn$</em>{1.96}$O$_4$</td>
<td>+ 3.58</td>
<td>–</td>
<td>Sol-gel, calcination in air 300 °C/48 h and 600 °C/24 h + quench</td>
</tr>
<tr>
<td>Q650</td>
<td>Li$<em>{0.983}$Mn$</em>{1.97}$O$_4$</td>
<td>+ 3.56</td>
<td>–</td>
<td>Sol-gel, calcination in air 300 °C/48 h and 650 °C/24 h + quench</td>
</tr>
<tr>
<td>Q700</td>
<td>Li$<em>{0.989}$Mn$</em>{1.98}$O$_4$</td>
<td>+ 3.54</td>
<td>–</td>
<td>Sol-gel, calcination in air 300 °C/48 h and 700 °C/24 h + quench</td>
</tr>
<tr>
<td>Q800</td>
<td>LiMn$_2$O$_4$</td>
<td>+ 3.5</td>
<td>$a$ = 0.82517(7)</td>
<td>Sol-gel, calcination in air 300 °C/48 h and 300 °C/24 h + quench</td>
</tr>
<tr>
<td>Q850</td>
<td>LiMn$<em>2$O$</em>{3.9}$</td>
<td>+ 3.45</td>
<td>–</td>
<td>Sol-gel, calcination in air 300 °C/48 h and 850 °C/24 h + quench</td>
</tr>
<tr>
<td>Q900</td>
<td>LiMn$<em>2$O$</em>{3.9}$</td>
<td>+ 3.4</td>
<td>$a$ = 0.5735(1) $c$ = 0.8612(3)</td>
<td>Sol-gel, calcination in air 300 °C/48 h and 900 °C/24 h + quench</td>
</tr>
</tbody>
</table>
Deconvolution procedure for the spinel lithium manganese oxides was conducted using a Grams/AI program from Galactic (Galactic Industries Co., Salem, NH). A 50/50% Lorenzian/Gaussian band shape for all bands was assumed and fixed. The number of bands, their initial frequencies, their bandwidths (FWHM—full width at half maximum), and their intensities were selected based on careful examination of the RS and IR spectra obtained at high resolution, as presented later in this work, using the lowest number of bands to obtain the best curve fitting to the experimental pattern. Deconvolution was performed for each of the samples by using these initial estimates.

Generalized two-dimensional correlation spectroscopy analysis (Generalized 2D-CS) of the RS spectra of these spinels was performed using a program named KG2D, which was composed by Dr Yan Wang (Kwansei—Gakuin University) that is working as an application of the program Grams/AI. The seven temperature dependent spectra were normalized, and the 2D correlation maps represent the average of these seven spectra.

3. Results

Fig. 1 shows the powder diffraction patterns of the lithium-manganese samples calcined at 300, 800, and 900 °C in air. For the samples S300 and Q800 only the cubic spinel phase can be observed. Sample S300 (Li$_{0.96}$Mn$_{1.92}$O$_4$) shows very broad diffraction peaks due to defected structure and low crystallinity. Calculated lattice constant (a) equals 0.8173(2) nm and this is the value consistent with those observed for the spinels with defected cations sublattices [24,25]. Calcination at higher temperatures improves crystal structure and increases the size of crystallites. The observed diffraction lines are more intense and narrow. The high lattice constant (a = 0.82517(7) nm) of the sample Q800 (LiMn$_2$O$_4$) proves well-defined stoichiometry and structure of LiMn$_2$O$_4$. During calcination a sintering of the sample was also observed. The BET surface areas versus the calcination temperatures are presented in Fig. 2. XRD pattern of Q900 sample (LiMn$_2$O$_{3.9}$) shows appearance of a tetragonal phase (a = 0.5735(1) nm, c = 0.8612(3) nm). Such a formation of new tetragonal spinel phase was previously reported by Tarascon [26] and identified as to be LiMn$_2$O$_{3.84}$. In Table 2 the in situ XRD measurements of the S300 sample are presented [6]. The temperature dependence of the lattice parameter showed complex variation with heating (Fig. 3). One may distinguish three regions with different slope. Two of them, RT-450 °C and 700–850 °C, are related to various coefficients of thermal expansion of the sample. The coefficient of thermal expansion at higher temperatures (700–850 °C) is about one order higher than for the low temperature region. This is consistent with observed arrangement of spinel structure during high temperature calcination (see results of MS-TGA/SDTA measurements presented below), because well-defined close-packed spinel structure should reveal higher coefficient of thermal expansion than defected material with cations vacancies.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.8173(2)</td>
</tr>
<tr>
<td>300</td>
<td>0.8177(1)</td>
</tr>
<tr>
<td>400</td>
<td>0.8179(1)</td>
</tr>
<tr>
<td>450</td>
<td>0.8187(1)</td>
</tr>
<tr>
<td>500</td>
<td>0.8217(1)</td>
</tr>
<tr>
<td>550</td>
<td>0.8223(1)</td>
</tr>
<tr>
<td>600</td>
<td>0.82283(7)</td>
</tr>
<tr>
<td>650</td>
<td>0.82362(6)</td>
</tr>
<tr>
<td>700</td>
<td>0.82367(6)</td>
</tr>
<tr>
<td>750</td>
<td>0.82500(5)</td>
</tr>
<tr>
<td>800</td>
<td>0.82588(7)</td>
</tr>
<tr>
<td>850</td>
<td>0.82725(5)</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern of S300, Q800 and Q900.

Fig. 2. Surface area BET as function of calcination temperature.

Fig. 3. In situ lattice constant as function of calcination temperature.
To determine the chemical composition of the sample and reactions taking place during calcination, the MSTGA/SDTA measurements were performed. The examples of thermogravimetric experiments with S300, Q800, and Q900 samples obtained at temperature increase with the speed of 2.5 °C/min within the range of 30–1200–30 °C, are shown in Fig. 4. The data were normalized in relation to the mass of the sample S300 showing the perfect reversibility. The observed changes in mass of the samples resulted only from the loss or uptake of oxygen which was confirmed by analysis of the evolved gas (EGA) during the experiment. In Table 3 the calculated and observed mass changes during calcinations in the air of S300 sample were compared. The changes of mass of the sample S300 between 390 and 820 °C in the air are related to arrangement of the structure accompanied by the disappearance of cations vacancies and by the formation of the stoichiometric LiMn2O4. In this case it can be described (according to Kroger–Vink-Notation) by the Eq. (1):

$$\text{Li}_{0.96}V_{(V_{Li})0.04}\text{Mn}_{1.92}(V_{Mn})_{0.08}\text{O}_4 \rightarrow 0.96\text{LiMn}_2\text{O}_4 + 0.08\text{O}_2$$

In the range of 820–925 °C a reversible shift of equilibrium (2), with formation or disappearance of the oxygen vacancies, is observed.

$$\text{LiMn}_2\text{O}_4 \leftrightarrow \text{LiMn}_2\text{O}_{3.85}(V_{O})_{0.15} + 0.075\text{O}_2$$

Above 925 °C, another reversible decomposition takes place even in the air with formation of Mn3O4 and LiMnO2 and release of oxygen according to reaction (3):

$$3\text{LiMn}_2\text{O}_{3.85}(V_{O})_{0.15} \leftrightarrow \text{Mn}_3\text{O}_4 + 3\text{LiMn}_2\text{O}_2 + 0.775\text{O}_2$$

The shape of TGA curves for Q800 and Q900 samples in the air is consistent with expectations based on the above presented Eqs. (2) and (3).

The Raman spectra, in the frequency range of 300–800 cm⁻¹, of S300, Q600, Q650, Q700, Q800, Q850, and Q900 spinels calcined at various temperatures are shown in Fig. 5. These spectra are similar to those reported earlier by Ammudsen et al. [21] and Julien et al. [22], but different from the spectra given recently by Paolone et al. [20]. The last authors suggested a thermal decomposition of the spinel samples during the collection of the Raman spectra due to laser heating; the authors in their measurements used a very strong radiation (500 kW/cm²) at 632.8 nm laser line that is near the resonance band. The authors suggested that the correct Raman spectrum of LiMn2O4 should contain a broad band at 580 cm⁻¹ with two poorly defined features in the 300–400 cm⁻¹ range and no spectral feature at around 650 cm⁻¹. In the present measurements, much lower energy of the laser (32 W/cm²) was used and the Raman spectra were collected in the KBr discs to avoid sample degradation. In addition, to prove that the spinel samples do not undergo thermal degradation during Raman spectra collection, the IR spectra of the same samples, but dissolved only by ~5 times, were measured. Fig. 6 presents the IR spectra collected at room temperature for lithium-manganese spinels calcined at various

![Fig. 4. Thermogravimetric analysis of S300, Q800 and Q900.](image-url)

![Fig. 5. Raman spectra of S300–Q900 spinels.](image-url)

![Table 3 Observed and calculated mass changes during calcinations of the S300 sample](table-url)
temperatures. The IR spectra of the samples after Raman measurements were similar to those obtained for the samples not exposed to laser radiation (before Raman experiments) and they are similar to the spectra reported previously [22,27]. It proves that our samples do not undergo any remarkable decompositions during the Raman measurements, as opposite to the data reported in Ref. [20].

The Raman spectra presented in Fig. 5 are dominated by two bands observed at 626 and 656 cm⁻¹ and show changes in relative intensities of these bands, especially for the 656 cm⁻¹ band. This band of the A₁g symmetry results from the symmetric Mn-O stretching vibrations (ν_{sym}(Mn–O)) of MnO₆ groups and shows a small shift towards lower energies in series from S300 to Q900. This observation suggests a decrease in the strength constant of the Mn-O bond (increase of the length bond). This is consistent with the observed increase in the lattice constant (Table 1). The second mentioned band (656 cm⁻¹) was assigned to the asymmetric Mn-O stretching (ν_{asym}(Mn–O)) vibration of the MnO₆ octahedron [21,22,28]. It should be excluded for the perfect spinel structure (Fd3m), in the both RS and IR spectra; however, decrease of the symmetry can make it active.

The integral intensities of these two bands, i.e. ν_{sym}(Mn–O) and ν_{asym}(Mn–O) calculated from the Raman spectra, vary among the series of spinels were observed (Fig. 7). The highest intensity of the A₁g (626 cm⁻¹) band was observed for stoichiometric Q800 spinel shows, while the A₂u (656 cm⁻¹) band shows the lowest intensity. The opposite relation was observed for the S300 sample. Similar dependences of the integral intensity of the phonon lines were observed for the IR spectra (Fig. 7). These relations are in accordance with concentration of defects in the spinels investigated here (Table 4).

To determine the influence of calcination on the local structure of the lithium-manganese spinels 2D-correlation spectroscopy [29–33] was applied using changes of the calcination temperature as a variable. Fig. 8 presents (a) synchronous and (b) asynchronous 2D-correlation spectra in the frequency range of 540–730 cm⁻¹ generated from the temperature dependent (300–900 °C) Raman spectra of the spinel samples. The synchronous Raman spectrum contains one strong and one-low intensity auto-peaks observed at 656 and 626 cm⁻¹, respectively. These peaks correspond to the modes described above, the ν_{asym}(Mn–O) and ν_{sym}(Mn–O) vibrations of the MnO₆ groups, respectively. The strong intensity of 656 cm⁻¹ peak suggests that the intensity of this band changes significantly with the temperature. In addition to the auto-peaks one negative cross-peak at (626, 656) cm⁻¹ is present in the synchronous spectrum. The negative sign of this cross-peak indicates that the 626 and 656 cm⁻¹ bands show

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**Table 4**

Relation between the amount of the defects and integral intensity of the Raman and IR spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Mn⁴⁺]</th>
<th>[Mn³⁺]</th>
<th>[Mn⁴⁺]:[Mn³⁺] ratio</th>
<th>Amounts of defects (mole)</th>
<th>Relative integral intensity of the phonon lines (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Vᵢ</td>
<td>Vₘₐ</td>
</tr>
<tr>
<td>S300</td>
<td>0.65</td>
<td>1.27</td>
<td>0.52</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>Q600</td>
<td>0.82</td>
<td>1.14</td>
<td>0.72</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Q650</td>
<td>0.87</td>
<td>1.10</td>
<td>0.79</td>
<td>0.015</td>
<td>0.03</td>
</tr>
<tr>
<td>Q700</td>
<td>0.91</td>
<td>1.07</td>
<td>0.85</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Q800</td>
<td>1.1</td>
<td>1.1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Q850</td>
<td>1.1</td>
<td>0.9</td>
<td>1.22</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Q900</td>
<td>1.2</td>
<td>0.8</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
the temperature dependent intensity changes in the reverse direction. On the other hand, the asynchronous Raman spectrum develops three cross-peaks at (619, 626), (626, 646), and (639, 656) cm$^{-1}$. The appearance of these peaks in the asynchronous spectrum suggests that the directions of the transition moments of these modes are different. The positive sign of the (619, 626) cm$^{-1}$ band points out that temperature-induced spectral changes take place earlier at 619 cm$^{-1}$ than those at 626 cm$^{-1}$. On the other hand, the negative sign of the last two peaks suggests that spectral changes take place earlier at 646 cm$^{-1}$ than those at 626 cm$^{-1}$, and at 656 cm$^{-1}$ than those at 639 cm$^{-1}$.

The DSC measurements of the spinel samples are shown in Fig. 9a. The samples S300 and Q600 do not show any heat effects which may be interpreted as a low temperature phase transition from cubic to orthorhombic structure. For the samples: Q650, Q700, and Q800 changes are observed on cooling and heating cycles resulting in a hysteresis of about 15°C. These effects are related to the low temperature phase transition. These changes appear within the same temperatures range as that for DSC curves (Fig. 9a). The sample Q900 shows the highest electrical conductivity with the lowest activation energy of electrical conductivity ($E_a$) (Fig. 9b). This is related to its tetragonal structure that is characterized by lower Mn–Mn distance.

4. Discussion

Analysis of thermal and electrical properties at about room temperature (Fig. 9a, b) shows a correlation (Fig. 10) between observed enthalpy ($\Delta H$) of phase transition and changes in electrical conductivity ($\Delta \log \sigma$) during this transformation. It suggests that lowering of electrical conductivity is caused by overcoming Jahn–Teller distortion of the Mn$^{3+}$ ions. We can conclude that the observed heat effect during phase transition relates to stabilisation energy obtained by a change in the electron states ($e_g^0 \rightarrow a_g^0$) of the Mn$^{3+}$ ion. A model of the phase transition from cubic to orthorhombic structure is presented in Fig. 11. For the Li–Mn spinels a small polaron conduction mechanism is
observed, thus, the activation energy \( E_a \) of electrical conductivity is equal to activation energy of the charge carrier migration (\( \text{Mn}^{3+} \rightarrow \text{Mn}^{4+} \)). In consequence, the changes in activation energy of electrical conductivity are related to changes in the lattice constant (Table 1).

Overcoming the Jahn–Teller distortion removes degeneration of the \( t_{2g} \) and \( e_g \) orbitals, resulting in the stabilisation energy \( (E_s) \) of the HOMO level, and the apparent activation energy of electrical conductivity of the \( \text{Mn}^{3+} \) ions becomes a sum of \( E_a + E_s \). This may by treated as a stronger localization of charge carriers, eliminating them from the electric charge transport. The number of effective carriers in the spinel is determined by \( [\text{Mn}^{3+}] \cdot [\text{Mn}^{4+}] \) product. It explains the increase of electrical conductivity with calcination temperature increase when not all \( \text{Mn}^{3+} \) ions participate in charge transport. The \( \text{Mn}^{3+} \) ions in polyhedra of lower symmetry seem to be excluded from the charge transfer process.

Jahn–Teller distortion of \( \text{Mn}^{3+} \) may only occur for \( \text{MnO}_6 \) with the \( O_h \) symmetry and high-spin configuration of \( \text{Mn}^{3+} \). Hence, one may assume that the heat effect accompanying the phase transition as well as the change in electrical conductivity must be proportional to concentration of such \( \text{Mn}^{3+} \) ions. Analysis of the changes in integral intensity of the symmetric and asymmetric stretching of the \( \text{Mn}–\text{O} \) bands in the \( \text{MnO}_6 \) octahedron (Fig. 7) leads to the conclusion that the highest concentration of high symmetric \( \text{Mn}^{3+} \) \( \text{O}_6 \) octahedrons should be present in the Q800 sample. Increase in number of cation defects (S300–Q700) or oxygen vacancies (Q850, Q900) that decreases intensity of the \( \text{Mn}–\text{O} \) symmetric stretching modes simultaneously with increase of the \( \text{Mn}–\text{O} \) asymmetric stretching modes (Table 4) causes lowering of the local symmetry. It results in suppressing or even elimination of the low temperature phase transition in the spinel. Such observations and correlations strongly confirm proposed model (Fig. 11).

5. Conclusions

The complementary studies of the lithium-manganese spinels (Li:Mn=1:2) showed that the conditions of their preparation have major influence on their physicochemical properties. The most important determinants of the process have been defined. The low temperature phase transition in the Li-Mn spinel may only occur if high ordered structure prevails, and high symmetry of the \( \text{MnO}_6 \) octahedron is essential here. The nature of this transformation is related to Jahn–Teller distortion of the \( \text{Mn}^{3+}\text{O}_6 \) octahedron. If so, to suppress the phase transition it is not necessary to change the \( \text{Mn}^{3+}/\text{Mn}^{4+} \) ratio which may affect the lower performance of the cathode material (the higher performance of cathode is reached when this ratio is close to 1). It seems to be enough to lower the high symmetry of the \( \text{MnO}_6 \) octahedron, for example by controlled formation of crystal defects or by izo-electronic substitution of oxygen in...
the anion sublattice by sulphur. The last peculiarity has been tested in a separate paper [34].

References