Stoichiometry Effects on the Electrical Conductivity of Lithium-Manganese Spinels

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The electrical conductivity of lithium-manganese spinels is analyzed in samples with different starting Li cationic fraction x. Li-rich spinels, resulting from Li-Mn substitution around the stoichiometric value ($x = 0.333$), show conductivity values higher than that observed in stoichiometric $LiMn_2O_4$. Besides, a conductivity drop, associated with a structural phase transition at about 290 K in $LiMn_2O_4$, progressively disappears by decreasing x, while it is absent in Li-rich samples. Stoichiometry effects on the concentration of charge carriers and on the available sites for the hopping transport process are evaluated, as well as the effects due to coexisting insulating phases. The role of the Jahn-Teller effect on the conductivity behaviour of stoichiometric and Li-poor spinels is also considered.

Key words: Electrical Conductivity; Lithium Manganese Oxides; $LiMn_2O_4$.

1. Introduction

$Li[Mn^{3+},Mn^{4+}]O_4$-type spinel compounds, henceforth written as $LiMn_2O_4$ compounds, show electrical properties which depend on electron hopping owing to the coexistence of different oxidation states of Mn ions, one of which is a Jahn-Teller ion (the $3d^4$ Mn^{3+} ion). A linear dependence of $\log(\sigma T)$ on $1/T$ was observed in $LiMn_2O_4$, as expected from a thermally activated hopping process, and a negative Seebeck coefficient confirmed the electronic character of the charge carriers [1]. An anomaly of $\sigma(T)$ at about 290 K in the linear Arrhenius plot, in form of a hysteresis loop [1, 2], was associated to a structural phase transition resulting from the onset of a cooperative Jahn-Teller (J-T) effect [1 - 6]. This transition disappears on increasing the Li content, even for a very small excess of Li with respect to the $LiMn_2O_4$ stoichiometry [4].

Compounds deviating from the $LiMn_2O_4$ stoichiometry can usefully be employed to influence the conductivity and to avoid the occurrence of structural phase transitions [3, 7, 8]. In this work we investigated the conductivity of samples containing $Li_{1+y}Mn_{2-y}O_4$ spinel phases with a wide range of Li stoichiometric deviation ($-0.36 < y < 0.16$) [9] together with suitable amounts of other insulating Mn oxides with the role of stoichiometry compensators.

A model relating the conductivity to variations of y and to the amount of insulating phases is proposed. The role of the J-T effect on the conductivity of Li-poor and stoichiometric spinels will also be discussed.

2. Experimental Procedure

Samples were prepared from the reactive system MnO/Li_2CO_3 (Alfa 99.9% and Carlo Erba R.P., respectively), the lithium cationic fraction, x, in the starting mixtures ranging between 0.10 and 0.53. Each mixture was fired in air for 8 h at 1073 K and 8 h at 1173 K. Both heating and cooling rates were 5 K/min. X-Ray diffraction (XRD) measurements were performed to detect the coexisting phases, and Rietveld profile refinement [10] was carried out to analyze the diffraction patterns, following a procedure previously described [11]. Samples in form of disks and bars were then obtained by sintering the pressed powders for 12 h at 1173 K in air.

Table 1. Weight % (s) and stoichiometry deviation (y) of the spinel phase in samples with different Li cation fraction (x) [9] and conductivity (σ) at room temperature.

x	s	y	$\sigma \cdot 10^4/\Omega^{-1}\mathrm{cm}^{-1}$
0.10	42.4	−0.36	0.47
0.20	69.5	−0.19	2.1
0.25	81.0	−0.11	2.7
0.31	89.0	−0.02	2.5
0.325	98.5	~0	4.2
0.333	100	0	5.0
0.35	100	0.04	5.6
0.38	92.9	0.06	3.5
0.40	91.5	0.09	2.15
0.44	78.0	0.09	0.40
0.53	44.3	0.16	< 0.01

Four-electrode dc conductivity measurements were performed by means of a SOLARTRON 1286 galvanostat/electrometer apparatus. Impedance spectroscopy measurements were also carried out, using a SOLARTRON 1255 or 1260 frequency response analyzer in the 10^{-3} - 10^7 Hz frequency range with a homemade high-impedance adapter (10^{12} Ω, 3 pF). A LEYBOLD ROK10 cryostat was used for the low-temperature measurements.

3. Results

In Fig. 1 the Arrhenius plot log (σT) *vs.* $1/T$ of 9 samples is shown. The σ values at room temperature of these and two more samples are reported in Table 1 together with the spinel percentage, s, and the lithium stoichiometry deviation of the spinel phase, y, as previously determined [9] by XRD, EPR and static magnetic susceptibility measurements. Samples with composition near that of the $LiMn_2O_4$ and obtained with $x < 0.333$ show a small step at about 290 K.

In Fig. 2 this behaviour near the transition temperature is shown in enlarged scale. An anomaly with a hysteresis loop (see inset for $x = 0.325$) is noted in the samples with $0.25 \leq x \leq 0.333$. Such an effect is not detectable in the samples with $x > 0.333$.

Figure 3 shows the dependence of σ on the lithium content x at a few representative temperatures. Near the stoichiometric composition ($x = 0.333$) a clear drop of σ is observed for $x < 0.33$ while a large decrease of σ appears at pronounced increases of x from 0.333. This behaviour is common to all temperatures. In particular, for $T > 290$ K, the drop of σ (compare samples with $x = 0.35$ and $x = 0.333$) is quite constant in the semilogarithmic plot.
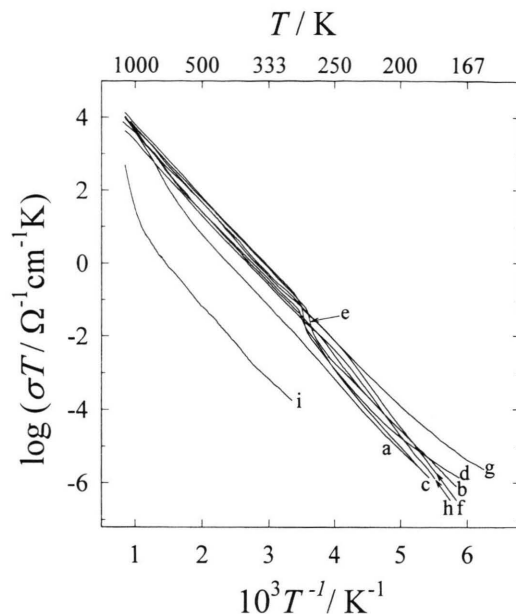

Fig. 1. Arrhenius plot of log (σT) *vs.* $1/T$ of the samples with x: a) 0.10, b) 0.20, c) 0.25, d) 0.325, e) 0.333, f) 0.35, g) 0.38, h) 0.40 and i) 0.53.
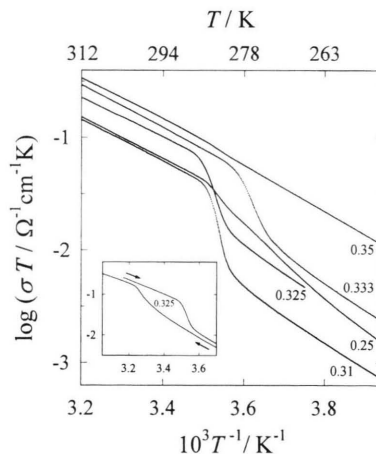

Fig. 2. Temperature dependence of the conductivity of representative samples with $0.25 \leq x \leq 0.35$ near the temperature of the structural transition observed at about 290 K in stoichiometric spinel. A hysteresis loop for $x = 0.325$ is shown in the inset.

Impedance spectroscopy measurements, showing a single half circle covering the entire frequency range, indicate that the resistivity values obtained by the four-probe dc technique must be attributed to bulk properties, so excluding grain-boundary contribution [1].
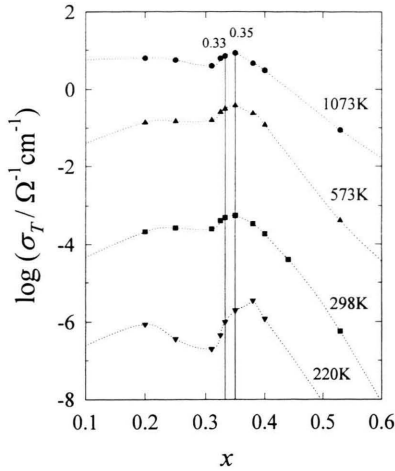
Fig. 3. Dependence of σ on the Li content x at a few representative temperatures.
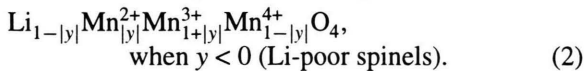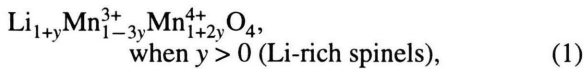
4. Discussion and Conclusions

Three facts are worth to be noted:

(i) the occurrence of the step-wise $\sigma(T)$ anomaly at 290 K has an "asymmetric" compositional dependence around $x = 0.333$, since the anomaly is not observed for $x > 0.333$ (Figure 2);

(ii) $\sigma(x)$ for $x \leq 0.333$ shows a decrease in samples near the stoichiometric spinel composition (Figure 3);

(iii) for $T > 290$ K the ratios between $\sigma(x)$ values with $x = 0.35$ and $x = 0.333$ are independent of the temperature (Figure 3).

It will be shown how these facts can be interpreted within a compositional model of Li/Mn spinels where Li substitutes for Mn when $x > 0.333$, and *vice versa* when $x < 0.333$ [9]. In other words, the composition of the generic spinel $Li_{1+y}Mn_{2-y}O_4$ may be regarded as arising from the following detailed formulae, previously discussed [9]

$$Li_{1+y}Mn^{3+}_{1-3y}Mn^{4+}_{1+2y}O_4,$$
$$\text{when } y > 0 \text{ (Li-rich spinels),} \tag{1}$$

$$Li_{1-|y|}Mn^{2+}_{|y|}Mn^{3+}_{1+|y|}Mn^{4+}_{1-|y|}O_4,$$
$$\text{when } y < 0 \text{ (Li-poor spinels).} \tag{2}$$

It must be remarked that this model describes the spinels produced by high temperature solid state reaction, while samples from electrochemical preparation usually possess a non-stoichiometry stabilized by cation or oxygen vacancies [7 - 9, 12].

Concerning point (i), the occurrence of the $\sigma(T)$ anomaly at 290 K reflects the presence of a structural

transition induced by cooperative J-T distortion of the oxygen octahedra around Mn^{3+} ($3d^4$) ions [1 - 6]. Thus, the "asymmetric" compositional dependence of the anomaly indicates that the Li-poor spinel lattice is quite compatible with the cooperative distortion, whereas Li-enrichment quickly inhibits this structural phase transition. This fact can be consistently explained within the substitutional model of the spinel structure applied to these samples. In this model, Li^+ ions in tetrahedral sites are substituted by Mn^{2+} ions when $x < 0.333$, and the charge compensation is achieved by the increase of the Mn^{3+}/Mn^{4+} ratio in octahedral sites. The lattice distortions expected from this substitution are very small because the ionic radii of Li^+ and Mn^{2+} in tetrahedral sites are rather similar (0.059 and < 0.067 nm [13], respectively). Thus the cubic symmetry of the coordination octahedra around the Mn^{3+} sites should be quite preserved, and a cooperative J-T static effect should still occur. In contrast, Li-rich samples do not show any trace of the 290 K anomaly. In fact, according to the same approach, a substantial modification of the lattice is expected from Li-enrichment of the spinel structure if this is achieved by substituting Mn^{3+} ions in octahedral sites by Li^+ ions, since their ionic radii are quite different (0.058 and 0.076 nm, respectively [13]). Moreover, Li-enrichment results in a dilution of the J-T ions in the lattice. Both effects are indeed strongly competitive to the occurrence of cooperative static J-T distortion, consistently with the experiment.

As now regards the conductivity drop observed in nearly stoichiometric samples with $x \leq 0.333$ (point (ii) and Fig. 3), the evaluation of the dependence of conductivity for the spinel phase only on the stoichiometry deviation y (Table 1), can be considered first.

For a hopping process,

$$\sigma = \frac{A}{T} \exp(-E_H/kT) \tag{3}$$

with $A = c(1 - c) \cdot NPe^2a^2\nu_0/k$, where e and k have the usual meaning, E_H is the activation energy for the hopping mechanism, ν_0 and a are the hopping frequency and the distance between sites for the hopping, P is a numerical factor equal to 1 in the adiabatic limit [14]. $Nc(1 - c)$ is the only factor sensibly dependent on the Mn stoichiometry, since c is the ratio between the number of charge carriers (corresponding to the Mn^{3+} sites) and the number N of available sites

for the hopping process (all octahedrally equivalent Mn sites), that is

$$c = \frac{1 - 3y}{2 - y}, \text{ when } y > 0, \qquad (4)$$

$$c = \frac{1 + |y|}{2}, \text{ when } y < 0. \qquad (5)$$

Therefore the dependence of σ on y for the spinel phase can be written in the form

$$\sigma_{\text{spinel}}(y) = \frac{\sigma_0}{N_0 c_0 (1 - c_0)} N(y) c(y)(1 - c(y)), \qquad (6)$$

where the subscript 0 refers to the stoichiometric spinel with $y = 0$. The y dependence can be made explicit by substituting (4) and (5) in (6) and taking into account that $N = 2 - y$ for $y > 0$ and $N = 2$ for $y < 0$, according to (1) and (2):

$$\sigma_{\text{spinel}}(y > 0) = 2\sigma_0(1 - 3y)\left(1 - \frac{1 - 3y}{2 - y}\right), \qquad (7)$$

$$\sigma_{\text{spinel}}(y < 0) = 2\sigma_0(1 + |y|)\left(1 - \frac{1 + |y|}{2}\right). \qquad (8)$$

A first indication of the anomalous behaviour of the stoichiometric spinel appears by comparing the experimental (Fig. 3) and expected conductivity values of the $x = 0.35$ ($y = 0.04$) and $x = 0.333$ ($y = 0$) samples, both free from spurious phases (see Table 1). From (7) the ratio σ_{spinel} ($x = 0.35$)/$\sigma_{\text{spinel}}(x = 0.333)$ should be 0.96. Consequently, the experimental σ value of the $x = 0.35$ sample being $5.6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$, the expected σ_0 value for the stoichiometric sample should be $5.83 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$, to be compared with the experimental value $5.0 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$. This difference, which reflects the drop of $\sigma(x)$ for $x = 0.333$ in Fig. 3, is about 16%, well above the experimental uncertainty.

The expected contribution to σ from the only spinel phase in the samples may also be expressed as a function of the spinel percentage, s, because a correlation between the y and s values in samples with different Li content can be found. In particular, the smaller the amount of spinel phase, the larger the Li-enrichment or Li-deficiency of the spinel phase itself (Table 1). This correlation is shown in Fig. 4: the behaviour followed by the experimental data is also consistent with the limit y values ($y = 0.33$ in Li-rich and $y = -1$ in
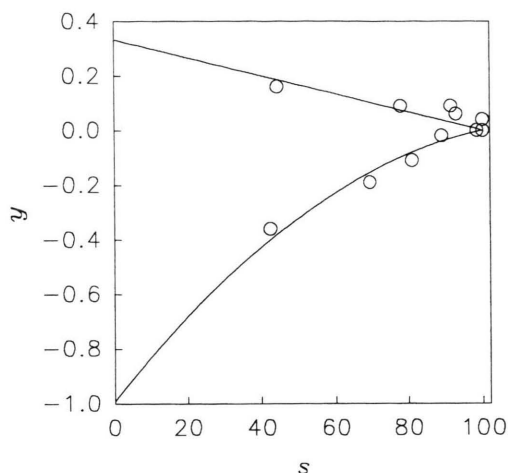

Fig. 4. Experimental correlation between y values and spinel percentage s in samples with different Li content. The curves are obtained by fitting the data with polynomials at the limit y values of the compositional model.

Li-poor spinels) in the compositional expressions (1) and (2). Empirical $y(s)$ relations obtained by fitting the data of Fig. 4 and inserting in (7) and (8) allow one to report in Fig. 5, together with the experimental σ values, the expected $\sigma_{\text{spinel}}(s)$ behaviour of the only spinel phase.

Another effect on σ comes from the insulating phases that block the conduction path. A percolation regime is expected proportional to $(s - s_c)^2$ for spinel concentrations s close to a critical value $s_c \sim$ 25% [15, 16] whereas a linear behaviour should be followed at larger s values. In Fig. 5 curves are shown for the two expected regimes:

$$\sigma(s) \propto \sigma_{\text{spinel}}(s)[s - s_c]^2, \quad \sigma(s) \propto \sigma_{\text{spinel}}(s)s. \qquad (9)$$

The linear regime is well-verified in Li-rich samples with $s > 85\%$. For Li-poor samples, the deviation of $\sigma(s)$ from the linear trend for high spinel concentrations confirms that other mechanisms influence the conductivity in this compositional region.

Since the spinel stoichiometry deviation affects only the pre-exponential term of σ in (3), the difference between the experimental σ values and the general trend in Fig. 5, related to the conductivity drop for $0.31 \leq x \leq 0.333$, may depend on the activation energy for the hopping process. So, it can be supposed that the behaviour of samples subjected to the J-T effect arises from a difference Δ in the hopping energy:
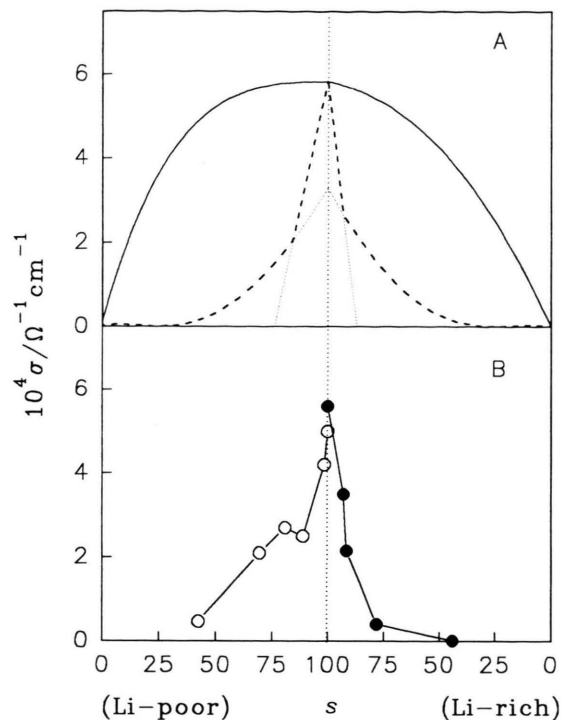
Fig. 5. (A) Expected $\sigma_{\text{spinel}}(s)$ behaviour (solid line) at room temperature of the only spinel phase, from (7) and (8) and from data in Fig. 4, together with the percolative and linear conductivity regimes (dashed lines) according to (7), (8), and (9). (B) Experimental σ values (filled symbols for the Li-rich samples) at room temperature.

$$\sigma = \frac{A}{T} \exp(-(E_{\text{H}} + \Delta)/kT). \tag{10}$$

Figure 6 reports the temperature dependence of Δ obtained by analyzing the conductivity drop near $x = 0.333$. A linear behaviour $\Delta \propto kT$, as a consequence of point (iii), is followed above the temperature of the onset of a static cooperative J-T effect. This is just what can be expected from a process controlled by the statistics of vibrational modes at sufficiently high temperature. Then, a thermally activated process is clearly suggested as responsible for the lowering of conductivity in stoichiometric or quasi-stoichiometric samples with small Li-deficiency. Moreover, an energy gap of about 0.02 eV is deduced from the conductivity data below room temperature (Figure 3). This energy gap, within the same approach, should be consistent with the energy splitting between the states
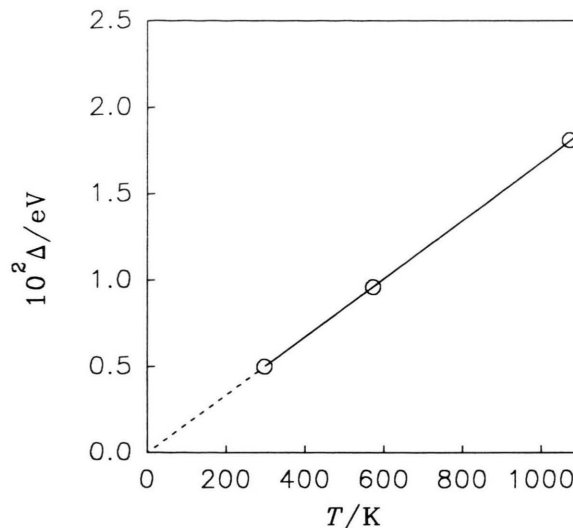

Fig. 6. Temperature dependence of Δ obtained by analyzing the conductivity drop near $x = 0.333$ at different temperatures above the onset of the static J-T effect.

involved in the static J-T effect, which should result in an increase of the energy barrier for the electron hopping. When carrying out crystal field calculations of the energy levels of the Mn^{3+} d-multiplet, and supposing a tetragonal elongation of the coordination octahedra consistent with the unit cell distortion at the structural transition (about 1.01 [4, 6]), a lowering of the $3z^2 - r^2$ energy level of the e_{g} doublet of about 0.03 eV was obtained.

In conclusion, it was shown that the conductivity behaviour of the investigated samples depends on the stoichiometric deviation y of the spinel phase and on the relative amount of the insulating phases, strictly related to the Li-enrichment and Li-deficiency of the spinel phase. In stoichiometric or quasi-stoichiometric samples with small Li-deficiency, the static (below 290 K) and dynamic (above 290 K) J-T effect appears to be competitive to the hopping transport mechanism by affecting the value of the activation energy E_{H}.

Acknowledgements

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