

# Comparative study of the phase transition of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ by anelastic spectroscopy and differential scanning calorimetry

A. Paolone<sup>a,b,\*</sup>, R. Cantelli<sup>a</sup>, B. Scrosati<sup>c</sup>, P. Reale<sup>c</sup>, M. Ferretti<sup>d,e</sup>, C. Masquelier<sup>f</sup>

<sup>a</sup> *Università di Roma “La Sapienza”, Dipartimento di Fisica, Piazzale A. Moro 2, I-00185 Roma, Italy*

<sup>b</sup> *Laboratorio Regionale SuperMat, CNR-INFN, Salerno, Italy*

<sup>c</sup> *Università di Roma “La Sapienza”, Dipartimento di Chimica, Piazzale A. Moro 2, I-00185 Roma, Italy*

<sup>d</sup> *Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, I-16146 Genova, Italy*

<sup>e</sup> *Laboratorio Regionale LAMIA, CNR-INFN, Corso Perrone 24, I-16152 Genova, Italy*

<sup>f</sup> *Université de Picardie “Jules Verne”, Laboratoire de Réactivité et de Chimie des Solids, F-80039 Amiens Cedex, France*

Received 5 October 2005; received in revised form 24 October 2005; accepted 24 October 2005

Available online 1 December 2005

## Abstract

$\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  is one of the most promising candidates as high performance cathode for lithium ion batteries. The stoichiometric compound is known to undergo a phase transition around room temperature, which has been widely studied and attributed either to Jahn–Teller effect or to charge ordering. For the applications it is important to suppress this phase transition, which lowers the electrochemical performances of the material. DSC measurements, which have been largely used in the literature to study the occurrence of the transformation, can detect a phase transition accompanied by latent heat only for  $x < 0.04$ . This fact has been generally accepted as a proof that the transformation is suppressed by doping. However, by using a technique extremely sensitive to rearrangements of atoms in the lattice, such as anelastic spectroscopy, we show that the phase transition persists up to  $x = 0.08$ , is shifted to lower temperatures, and changes its nature from first to higher order. The implications for the mechanism driving the transition and the similarities and differences with doped  $\text{Fe}_3\text{O}_4$ , which is the prototype of charge order transitions, are discussed.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Anelastic spectroscopy; Differential scanning calorimetry; Lithium ion batteries; Phase transition

## 1. Introduction

$\text{LiMn}_2\text{O}_4$  has attracted considerable interest over the last years both because of its practical importance as advanced cathode in rechargeable lithium ion batteries [1] and of the basic interest associated to the occurrence of a phase transition near room temperature which has been reported to correspond to a freezing of  $\text{Mn}^{3,2+}$  and  $\text{Mn}^{4+}$  ions in an ordered array, that is a charge order transition [2]. The occurrence of this transition negatively affects the

electrochemical properties of the material. This explains why the phase transition occurring in the stoichiometric material has been widely studied. Most commonly techniques such as neutron [2] and X-ray diffraction [3,4], resistivity [2], differential scanning calorimetry (DSC) [4] infrared spectroscopy [5] and anelastic spectroscopy measurements [6] have been used to study this effect. All revealed thermal hysteresis along the phase transformation, which is typical of a first-order character.

Various substitutions of Mn with different ions (such as Cr, Co, Mg and Li) were exploited in order to suppress the phase transition or to shift it out of the working temperatures of the devices. It has been reported that on progressively doping the transition temperature decreases until the transition

\* Corresponding author. Tel.: +39 06 49914400; fax: +39 06 4957697.

E-mail addresses: [annalisa.paolone@roma1.infn.it](mailto:annalisa.paolone@roma1.infn.it), [paolone@roma1.infn.it](mailto:paolone@roma1.infn.it) (A. Paolone).

itself disappears [7]. However, in the most of the cases, those conclusions were drawn only on the basis of DSC results, as for  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  [8,9],  $\text{LiMg}_x\text{Mn}_{2-x}\text{O}_4$  [10] and  $\text{Li}_y\text{Mn}_{2-x}\text{Fe}_x\text{O}_4$  [11]. Precisely, such experiments show that on doping the transition temperature decreases from about 300 K at  $x = 0$  to 210 K at  $x = 0.04$ , and concomitantly the latent heat of transformation decreases until it vanishes for  $x = 0.04$ . This observation was interpreted as an evidence of the absence of the phase transformation at higher dopings [8,10].

In the present paper, we demonstrate that DSC alone is not sufficient to provide a correct answer to the problem. Indeed, by testing  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  with anelastic spectroscopy, i.e. a technique extremely sensitive to rearrangements of atoms in the lattice, we show that the transition is not suppressed by doping, at least at the levels so far reported. Indeed whilst DSC cannot detect a latent heat for a doping  $x \geq 0.04$ , thus letting to assume the suppression of the transition [8], anelastic spectroscopy reveals that a phase transformation still persists even at  $x = 0.08$ , which is the highest doping considered in the present work. In addition, these results, suggest that the phase transition progressively changes from first to higher order. We think that these new observations have important implications not only in terms of a correct evaluation of the practical potentiality of the lithium manganese spinel in the advanced lithium battery technology, but also in view of a better understanding its basic properties. Accordingly, the data obtained in this work are analysed with the aim of shading more light on the nature of the transition.

## 2. Experimental

$\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  powders ( $x = 0.00, 0.02, 0.04, 0.06$  and  $0.08$ ) were prepared by three subsequent solid-state reactions in air, each one of 10 h at 800 °C starting from  $\text{Li}_2\text{CO}_3$  and  $\text{MnOOH}$ . After each solid state reaction the powders were carefully ground. X-ray diffraction patterns show that the unit cell parameter decreases monotonically with  $x$ , as a result of the progressive increase of the average oxidation state of Mn; moreover, the patterns did not reveal any spurious phase. The powders were sintered for 40 h at 850 °C in an  $\text{O}_2$  atmosphere, in order to obtain bars 25–50 mm long, 5 mm wide and 1 mm thick for anelastic spectroscopy measurements.

The complex modulus  $E = E' + iE''$  was measured as a function of temperature by electrostatically exciting the lowest odd and the third flexural modes. The vibration amplitude was detected by a frequency modulation technique. The dynamical Young's modulus  $E'$  was obtained from the vibration frequency ( $f \propto \sqrt{E'}$ ), while the elastic energy loss coefficient  $Q^{-1}(T) = E''/E'$  [12] was measured by the amplitude decay of the free oscillations or the width of the resonance peak.

Small parts of the bars used for anelastic spectroscopy measurements having a mass of about 10–15 mg, were used for differential scanning calorimetry measurements

performed between 120 and 370 K by means of a Mettler-Toledo DSC822 system.

## 3. Results and discussion

Fig. 1 presents the DSC curves for the five samples between 150 and 370 K, both on heating and cooling with a rate of 10 K/min. A well-defined peak around room temperature is observed in the stoichiometric compound ( $x = 0$ ), which shows a clear thermal hysteresis of about 13 K ( $T_t \approx 292$  K on cooling and 279 K on heating). The sample with  $x = 0.02$  displays a much smaller peak, which however is broader than that of the undoped sample; it is shifted to lower temperatures (about 250 K), and presents also a smaller hysteresis ( $\sim 8$  K). At higher dopings, we could not detect any sharp feature ascribable to the latent heat of the phase transition, in agreement with previous measurements [8]. The results obtained by means of DSC are usually interpreted as the evidence of the suppression of the phase transition for  $x > 0.04$ . However, the DSC measurements are ambiguous; indeed the latent heat of the transition progressively decreases as  $x$  increases, so that at high dopings one cannot discriminate between the real suppression of the transition and its transformation into a higher order one, which is expected to display no latent heat. The possible survive of the phase transition at high dopings is important both from a fundamental point of

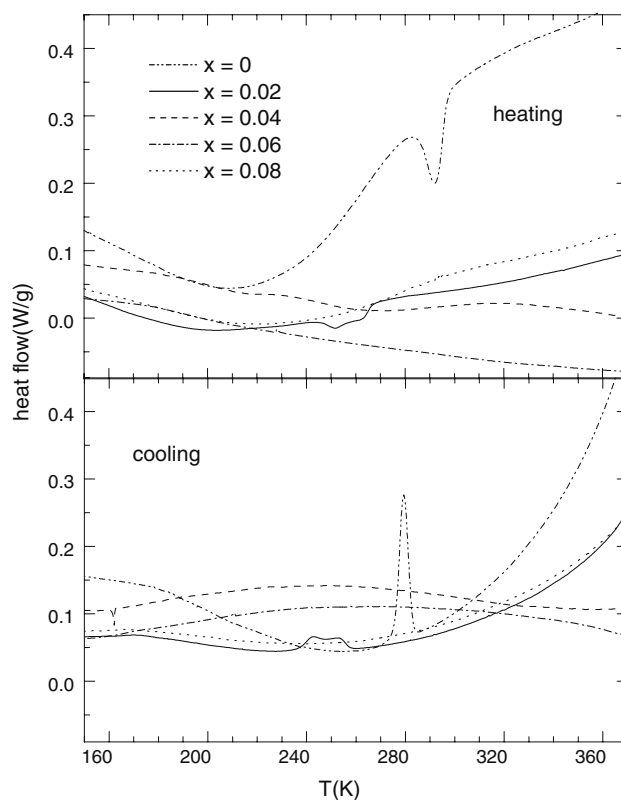


Fig. 1. DSC curves as a function of doping measured on heating (upper panel) and on cooling (lower panel) with a constant temperature rate of  $\pm 10$  K/min.

view and for the application of spinels to lithium batteries; indeed one of the explanation proposed for the decrease of the performances of the batteries after a number of charge/discharge cycles is that during Li insertion a possible over-reduction of Mn oxidation state at the electrode surface can occur, thus determining a local distortion. This is actually the reason for the interest in non-stoichiometric compounds, which should assure an oxidation state higher than 3.5 during the whole electrochemical process. In this context, also the physical and chemical properties of different composition from the nominal ones should be known.

To further investigate this problem, we measured the same samples of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  by means of anelastic spectroscopy. This spectroscopy and ultrasonic attenuation, which is its high frequency analogue, are well-established experimental techniques which have been widely used to study the occurrence of structural phase transitions because of their high sensibility to structural modifications, independently of the order of the transition [12,13].

Fig. 2 shows the coefficient of elastic energy dissipation and the modulus variation (referred to room temperature) as a function of temperature at a rate of about 0.2 K/min, carried out on the same  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  samples used for the DSC measurements. This low temperature rate is needed in order to follow the large variation of the fre-

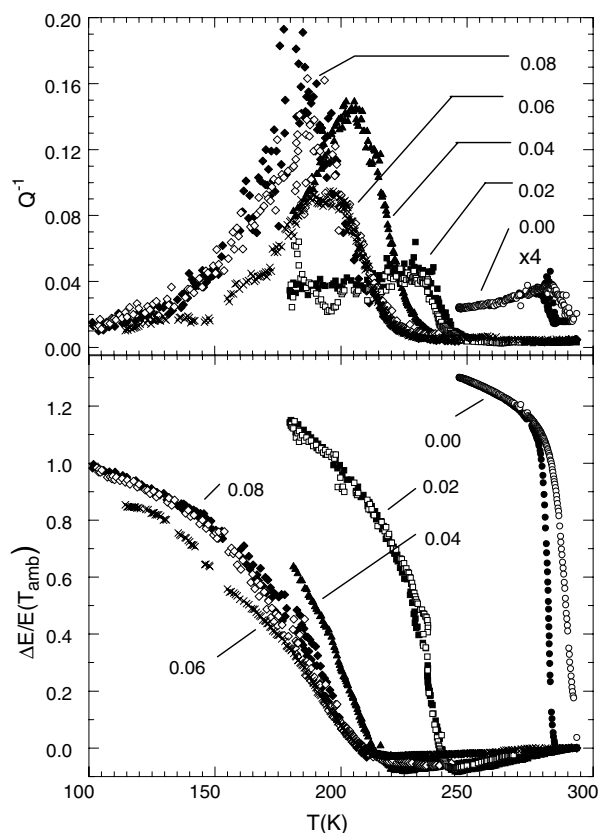


Fig. 2. Temperature dependence of the elastic energy loss function and of the variation of the Young's modulus respect to room temperature as a function of doping. Full (empty) symbols refer to measurements performed on cooling (heating).

quency which accompanies the phase transition. On cooling the  $x = 0.00$  sample (stoichiometric compound), a strong modulus inflection starting around 287 K is observed in the temperature range in which the charge order transition manifests itself as observed with DSC; at the same temperature, the concomitant measurement of dissipation presents a sharp increase. On heating, a hysteresis of about 10 K is visible both in the  $Q^{-1}$  and in the frequency curves. Those results are in good agreement with our previous study in a sample produced using  $\text{MnO}_2$  instead of  $\text{MnOOH}$  as the Mn precursor. The high value of  $T_t$  confirms the good stoichiometry of the specimen.

In the sample with  $x = 0.02$ , the modulus inflection starts on cooling at 242 K, i.e. 35 K below the transition of the  $x = 0.00$  compound, and the former temperature is very close to the temperature at which the DSC peak was measured for the same composition. The abrupt increase of dissipation starts at the same temperature of the modulus inflection, as in the  $x = 0.00$  sample, but its rise is 20 times higher with respect to  $x = 0$ . The temperatures of the  $f$  and  $Q^{-1}$  inflections agree with those of the DSC excitations and therefore they are ascribed to the onset of the phase transition. The modulus and the dissipation curves are retraced on heating, indicating that there is no visible thermal hysteresis associated with the phase transformation. This observation is different from the results of DSC; however, it should be considered that anelastic spectroscopy measurements are conducted at cooling rates (0.2 K/min) 50 times slower than DSC measurements (10 K/min), and a high rate may amplify the possible occurrence of hysteresis.

On cooling the samples with  $x = 0.04$  and 0.06, the temperatures of the Young modulus inflections are further decreased and are found at  $T_t \sim 225$  and 215 K, respectively. Considering that the elastic constants are extremely sensitive to the formation of second phases, we attribute the slope change of the  $E$  curves to the occurrence of the phase transition. At  $x = 0.08$  the temperature of the  $E$  abrupt rise is no further decreased. The dissipation curves display the same trend of the  $f$  curves but, above  $x = 0.02$ , the respective inflection temperatures do not coincide.

One can wonder whether the large modulus variation can be connected to the huge dissipation peak displayed by the samples with  $x > 0.02$ , instead of being associated to the persistence of the phase transition. In the case of the  $x = 0.08$  sample a joint measure of the first and third flexural modes was performed (see Fig. 3). A small shift of  $Q^{-1}$  toward higher temperatures with increasing frequency can be detected. In Fig. 3, we report the best fit curves using the Fuoss–Kirkwood model

$$Q^{-1} = \frac{\text{const}}{T} \frac{1}{(\omega\tau)^\alpha + (\omega\tau)^{-\alpha}},$$

where  $\omega$  is the angular vibration frequency,  $T$  is the temperature,  $0 < \alpha < 1$ , and  $\tau$  is the relaxation time, which has been considered to follow the classical Arrhenius law:  $\tau = \tau_0 e^{E/kT}$ , being  $E$  the activation energy of the relaxation process. The analysis is limited to the high temperature side

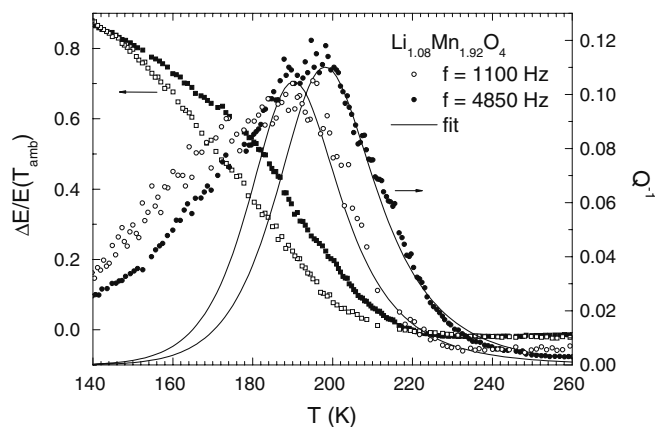


Fig. 3. Temperature dependence of  $Q^{-1}$  and of the variation of the Young's modulus of the  $x = 0.08$  at two different vibration frequency and best fit curves applying the Fuoss–Kirkwood model. The experimental data were obtained measuring the two modes seven month after the measure reported in Fig. 2.

of the dissipation peak, as the low  $T$  part cannot be reproduced by the Fuoss–Kirkwood model. The best fit parameters were  $\alpha = 0.5$ ,  $E = 7100$  K (0.61 eV) and  $\tau_0 = 10^{-20}$  s. The value of the relaxation time as derived from the peak shift with vibration frequency (due to the small difference of the temperature of the maximum of the dissipation in the measurements performed at the two vibration frequencies) is extremely low and actually unphysical. Therefore, the dissipation peak is not a simple thermally activated peak. Indeed, atypical values of the relaxation time have been largely found in different materials when a relaxation peak occurs at a temperature close to a phase transition [see Chapter 4 of [13]]. Considering these results we suggest that the phase transition persists even for  $x > 0.02$ . The value of  $E$  and  $\tau_0$  could be obtained even without performing a fit, just considering the shift of the maximum of the peak at different frequencies; therefore, the conclusions presently reported do not depend on the quality of the fit.

The comparison of the DSC and anelastic spectroscopy measurements indicates that the phase transition taking place around room temperature in the  $x = 0.00$  sample, shifts towards lower temperature with increasing  $x$  (oxidation state of Mn, as detected by X-ray diffraction), and for  $x = 0.08$ , it is found around 210 K, as shown by a marked modulus change. However, for  $x \geq 0.04$  the transition is not accompanied by any clear thermal effect, suggesting that the transition progressively changes from first to higher order. Those features are similar to those of  $\text{Fe}_3\text{O}_4$ , which is the prototype of charge order transformations. Indeed, as magnetite is doped with Zn or Ti (replacing Fe), or O vacancies the transition temperature progressively decreases while its nature changes from first to higher order [14]. This analogy persists also in the elastic properties; indeed measurements on  $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$  crystals [15] showed that  $c_{44}$  is the elastic constant which is more strongly affected by the transition. While for  $x = 0$ ,  $c_{44}$  and all the elastic constants  $c_{ij}$ , show a sharp positive step developing within 1 or 2 K, the doped samples display a V-

type increase of  $c_{ij}$  which extends in a much wider temperature range. This fact has been linked by the authors of [15] to the transformation of the transition from first- to second-order. In the present work, we report the temperature behaviour of the Young's modulus, which is a function of all the elastic constants: it is well evident from the experimental data that in the undoped sample there is a positive step at  $T_1$  on cooling, whilst the increase of  $E$  extends in a much broader temperature range for  $x \geq 0.04$ ; considering the results of [15] this fact is another indication of a change of the transition from a first-order to a second-order one, consistently with the indications obtained by the comparison of the DSC and anelastic spectroscopy measurements.

Anelastic spectroscopy is a powerful tool to detect eventual structural phase transformation; however, diffraction measurements are needed to identify the phases above and below the transition. In the previous paragraphs, due to the continuous evolution of the transition as a function of doping, it has been implicitly assumed that it marks the boundary between the same high temperature and low temperature phases reported for the stoichiometric compound [2]. However, the symmetry of the high- and low-temperature phases is irrelevant for the conclusions reported in the present paper.

In general, if a phase transition occurs one would expect changes in many physical properties at the transition temperature. In the case of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  very little information is available in the literature as a function of  $x$  and  $T$  [8,9,16,17]. Neither of these studies is directly in contrast with the results of the present one, because either the doping levels or the temperatures ranges previously investigated were different from ours. The magnetic susceptibility curve of  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  from 4 up to 300 K reported in [16], displays no features clearly attributable to a phase transition; however, this was the case also for the stoichiometric compound, for which a small signature of the phase transformation can be detected only in the derivative of  $1/\chi$ . Moreover, less dramatic effects are expected in a second-order phase transition than in a first-order one.

A last remark concerns the driving mechanism of the phase transition of  $\text{LiMn}_2\text{O}_4$ . It has been shown that below  $T_1$  this compound presents an ordered array of  $\text{Mn}^{3.2+}$  and  $\text{Mn}^{4+}$  ions, with well detectable distortions of the Mn–O octahedral [2]; however, it is still a matter of debate if the transformation into the orthorhombic phase is caused by the ordering of the charges or by the lattice distortions. Indeed the first diffraction studies of the structural phase transformation of the stoichiometric compound suggested that the transition was driven by the ordering of the lattice distortions caused by a Jahn–Teller mechanism [17]. This order–disorder scenario of the oxygen sublattice was confirmed quite recently by Akimoto et al. [18] on analyzing the X-ray diffraction pattern of a single crystal of this compound. Also EXAFS measurements [19] observed lattice distortions, which were even present in the high temperature phase. On the other hand, on the basis of a neutron diffraction study [2] it was asserted that the driving mecha-

nism should be due to the charge ordering, as it takes place simultaneously with the lattice distortions at the transition temperature in  $\text{LiMn}_2\text{O}_4$ , similarly to  $\text{Fe}_3\text{O}_4$  which is the prototype of charge order transitions.

A study of the transition as a function of doping may be effective to discriminate between the two mechanisms. Actually, it is well agreed that, if the transition was driven by the ordering of the charges caused by electrostatic interactions, it would disappear as soon as the mean valence of Mn deviates from 3.5. In fact, in  $\text{Fe}_3\text{O}_4$  the transformation seems to be prevented by a variation of 0.6% of the mean valence of Fe on the octahedral sites [14]. On the contrary, the present study shows that even with a formal valence of the manganese ions of  $\sim 3.6$  the phase transformation is still present. Therefore, further studies with additional spectroscopies are needed, even at higher dopings, in order to interpret the present phase transformation in  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ .

#### 4. Conclusions

A joint study of the same samples of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  has been conducted by means of DSC and anelastic spectroscopy. DSC measurements do not reveal heat exchange at higher dopings ( $x > 0.04$ ) generally leading to the conclusion that doping suppresses the phase transformation. Instead, anelastic spectroscopy, which is extremely sensitive to the lattice arrangement, provide clear evidence that the phase transformation persists up to  $x = 0.08$ , and that it is shifted towards lower temperatures while it changes its nature from first to higher order. The similarities and the difference with  $\text{Fe}_3\text{O}_4$ , which is the prototype of charge order transition, have been discussed.

#### Acknowledgements

We thank M. Del Bufalo, S. Gianoglio, M. Ottaviani for help in some of the anelastic spectroscopy experiments and M. Castellano for preliminary DSC measurements.

#### References

- [1] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [2] J. Rodriguez-Carvajal, G. Rouse, C. Masquelier, M. Hervieu, *Phys. Rev. Lett.* 81 (1998) 4660.
- [3] G. Rouse, C. Masquelier, J. Rodriguez-Carvajal, M. Hervieu, *Electrochem. Solid State Lett.* 2 (1999) 6.
- [4] G. Rouse, C. Masquelier, J. Rodriguez-Carvajal, E. Elkaim, J.P. Lauriat, J.L. Martinez, *Chem. Mater.* 11 (1999) 3629.
- [5] A. Paolone, P. Roy, G. Rouse, C. Masquelier, J. Rodriguez-Carvajal, *Solid State Commun.* 111 (1999) 453.
- [6] A. Paolone, R. Cantelli, G. Rouse, C. Masquelier, *J. Phys.: Condens. Mater.* 15 (2003) 457.
- [7] M. Wakihara, L. Guohua, H. Ikuta, T. Uchida, *Solid State Ionics* 86–88 (1996) 907;  
T. Ohzuku, S. Takeda, M. Iwanaga, *J. Power Sources* 81–82 (1999) 90;  
B. Ammundsen, M. Saijful Islam, D.J. Jones, J. Rozière, *J. Power Sources* 81–82 (1999) 500;  
Y.P. Wu, E. Rahm, R. Holze, *Electrochim. Acta* 47 (2002) 3491;  
D. Capsoni, M. Bini, G. Chiodell, V. Massarotti, P. Mustarell, L. Linati, M.C. Mozzati, C.B. Azzoni, *Solid State Commun.* 126 (2003) 169.
- [8] A. Yamada, *J. Solid State Chem.* 122 (1996) 160.
- [9] R. Dziembaj, M. Molenda, *J. Power Sources* 119–121 (2003) 121.
- [10] R. Basu, R. Seshadri, *J. Mater. Chem.* 10 (2000) 507.
- [11] T. Tsuji, M. Nagao, Y. Yamamura, N.T. Tai, *Solid State Ionics* 154–155 (2002) 381.
- [12] A.S. Nowick, B.S. Berry, *Anelastic Relaxation in Crystalline Solids*, Academic Press, New York, 1972.
- [13] See for example, *Mechanical Spectroscopy  $Q^{-1}$* , *Trans. Tech. Pub.*, 2001 (Chapter 5).
- [14] See for example J.M. Honig, *J. Alloy. Compd.* 229 (1995) 24;  
F. Walz, *J. Phys.: Condens. Mat.* 14 (2002) R285.
- [15] H. Schwenk, S. Bareiter, C. Hinkel, B. Lüthi, Z. Kakol, A. Koslowski, J.M. Honig, *Eur. Phys. J. B* 13 (2000) 491.
- [16] Y. Shimakawa, T. Numata, J. Tabuchi, *J. Solid State Chem.* 131 (1997) 138.
- [17] A. Yamada, K. Miura, K. Hinokuma, M. Tanaka, *J. Electrochem. Soc.* 142 (1995) 2149;  
A. Yamada, M. Tanaka, *Mater. Res. Bull.* 30 (1995) 715.
- [18] J. Akimoto, Y. Takahashi, N. Jijima, Y. Gotoh, *Solid State Ionics* 172 (2004) 491.
- [19] H. Yamaguchi, A. Yamada, H. Uwe, *Phys. Rev. B* 58 (1998) 8.