Absence of phase transformation at low temperature in Co-doped LiMn$_2$O$_4$ samples

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The phase transition in spinel LiMn$_2$O$_4$ was investigated using powder synchrotron radiation diffraction. A transition from cubic (Fd$ar{3}$m) to orthorhombic (Fddd) was observed around $T = 220$ K. Increasing the average valence of Mn by doping Co into the [Mn$_2$O$_4$] framework, LiMn$_{1.9-x}$Co$_x$O$_4$, reduced the concentration of Mn$^{3+}$ ions, suppressed the Jahn–Teller distortion and the cubic phase was retained at low temperature.

Introduction

Lithium transition-metal (Co, Ni, Mn or V) oxides which are used as positive electrodes in secondary lithium batteries have extensively been studied over the past two decades. Amongst these materials, manganese oxides were found to be advantageous in terms of specific energy, non-toxicity and low cost. Lithium spinel LiMn$_2$O$_4$ is the most promising candidate for innovative lithium-ion (rocking chair) batteries. It is believed that lithium manganese oxides batteries will be used in cellular telephones, notebook PCs and electrical vehicles in the future. $^{1-4}$

Some problems for the commercial application of LiMn$_2$O$_4$ are rechargeable capacity and poor cyclability of the charge–discharge process in the region of 4 V. These could be due to lattice instability of LiMn$_2$O$_4$ with the critical concentration of Mn$^{3+}$ ions. LiMn$_2$O$_4$ shows cubic Fd$ar{3}$m symmetry at room temperature with an average manganese valence of 3.5. The Mn exists in Mn$^{3+}$ (tet$_g$ $e^6$) and Jahn–Teller active Mn$^{3+}$ (tet$_e$ $e^2$) configurations. Decreasing the temperature causes a structural phase transition around 280 K due to the Jahn–Teller distortion in the Mn$^{3+}$O octahedra and the crystal structure of LiMn$_2$O$_4$ changes from cubic (Fd$ar{3}$m) to tetragonal (space group; I4$_1$/amd). $^{5-9}$ Oikawa et al. $^{10}$ showed that the reflections of the low temperature (LT) phase in its neutron and X-ray diffraction patterns were indexed not on the basis of a tetragonal unit cell but roughly on an orthorhombic one (space group; Fddd) with lattice parameters $a = 8.2797(2)$, $b = 8.2444(3)$ and $c = 8.1981(2)$ Å. Therefore, the diffraction pattern of the orthorhombic phase is very similar to their LT X-ray diffraction pattern. More recently, many studies have demonstrated that LiMn$_2$O$_4$ has the orthorhombic phase at low temperature. $^{11-14}$ Rodriguez-Carvajal et al. $^{15}$ on the basis of neutron and electron diffraction studies proposed an orthorhombic supercell with space group Fddd and $\pm 3 \times 3 \times 1$ axes with respect to the cubic value.

Several studies have been aimed at improving the material properties of LiMn$_2$O$_4$ and its efficiency in maintaining electro-chemical capacity, over a large number of cycles without sacrificing initial reversible capacity, and also its performance at low or high temperatures. Doping the Mn (16d) sites with a lower valent cation is a possibility because it reduces the Mn$^{3+}$ content and stabilizes the cubic structure in the face of Mn$^{3+}$ Jahn–Teller distortion. $^{15,16}$ Yamada $^8$ has shown that the substitution of Li$^+$ ions at the Mn site, Li(Li$_{1-x}$Mn$^{3+}_x$)O$_4$, increases the average ionic valence of Mn, thus decreasing the number of Jahn–Teller Mn$^{3+}$ ions. When $x > 0.035$ the phase transition near room temperature was not observed.

Towards practical applications, it is desirable to have a composition which has no structural transition close to room temperature. In this paper we report the synthesis of LiMn$_{1.9-x}$Co$_x$O$_4$ ($x = 0$ or 0.1), wherein Mn has partially been replaced with Co. We also present our studies on the effect of temperature on the phase transition in LiMn$_2$O$_4$ and LiMn$_{1.9}$Co$_{0.1}$O$_4$.

Experimental

Samples of the system LiMn$_{2-x}$Co$_x$O$_4$ with $x = 0$ or 0.1 were synthesized by solid-state reaction of Li$_2$CO$_3$, MnO$_2$ and Co$_2$O$_3$. Well ground mixtures of the starting materials were heated at 800 °C in air for 24 h, followed by two treatments each of 24 h at 800 °C with intermediate grindings. Powder X-ray diffraction analyses were carried out with a SCINTAG (X1) diffractometer (Cu-Ko radiation, $\lambda = 1.5406$ Å) at 40 keV and 30 mA. Data for the Rietveld refinement were collected in the 2θ range 15–120° with a step size of 0.02° and a count time of 10 s per step. The program GSAS $^{17}$ was used for the Rietveld refinement in order to obtain the crystal structure parameters of LiMn$_{1.9}$Co$_x$O$_4$. Compositional analyses were performed by using an EDAX-DX4 energy dispersive X-ray spectrometer (EDS).

A series of patterns was recorded with synchrotron radiation ($\lambda = 1.3271$ Å) in a limited angular region at different temperatures. The Wiggler-A beamline of the synchrotron radiation research center (SRRC), Taiwan, has been designed for such experiments, where the concern is more with photon flux than resolution. The optical design follows a first mirror focusing the beam vertically and an asymmetrically cut and horizontally bendable perfect single crystal as the diffractive object monochromatizing and focusing the beam horizontally. The focusing mirror is an 800 mm long tangential bent and water-cooled silicon mirror with gold coating on the surface. A single crystal of Si(111) with about 10° asymmetric cutting was used to deliver the monochromatic beam. The optics is designed to focus the beam into a 0.2 × 1.8 mm spot size at the sample position, which is about 24 meters away from the source or 6 meters from the monochromator. The wavelength of the beam is 1.3271 Å. The Wiggler-A hutch is equipped with a conventional Huber 4-circle diffractometer operating in the vertical geometry to obtain the best angular resolution in the...
Table 1  Refined fractional atomic positions, unit cell and reliability factors (%) of LiMn$_{2-x}$Co$_x$O$_4$ ($x = 0$ or 0.1) having Fd3m space group at room temperature. The atomic positions are, Li (0.125, 0.125, 0.125), Mn (0.5, 0.5, 0.5), O (x, x, x).

| x  | Li 10$^4$ $U_{ij}$/Å$^2$ | Mn(Co) 10$^4$ $U_{ij}$/Å$^2$ | O x | 10$^4$ $a_f$/Å | $a$/Å | R$_p$ (%) | R$_wp$ (%) | $\chi^2$ | Mn–Mn Mn–Co O–Li–O
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Fig. 1  Conventional (Cu-Kα radiation, $\lambda = 1.5406$ Å) and synchrotron ($\lambda = 1.3271$ Å) powder XRD spectra of LiMn$_{2-x}$Co$_x$O$_4$ with $x = 0$ or 0.1 at room temperature.

vertical plane. Two sets of X-Z translation slits are positioned in front of the diffractometer to define the incident angular divergences in the vertical and horizontal directions. A 5 cm long ionic chamber is used to monitor the incident photon flux before the slits and a scintillation counter is positioned vertically in the direction of the beam right after the slits to monitor the transported beam by counting the air scattered photons. Right in front of the detector, another scintillation counter, are two sets of X-Z slits providing better receiving angular resolution and which also serve as an air scattering rejector.

A flat imaging plate (Fuji, 20 × 40 cm) was used as a 2-D area detector, which can collect diffraction data up to 80 degrees in 2θ. The diffraction pattern is read out by using a MAC IPR 520 off-line imaging plate scanner. The dynamic range is as high as 10$^6$. In this study, the sample was cooled by an APD cryostat; the temperature can be varied from 320 to 15 K.

The valence of Mn was determined by chemical titration. The samples were dissolved in an excess of 20 mL K$_2$C$_2$O$_4$ and 2 mL H$_2$SO$_4$ at around 65 °C maintained by a water bath to reduce all Mn$^{2+}$ to Mn$^{3+}$ (2 < n ≤ 4), and then the excess of C$_2$O$_4^{2-}$ ions in the solution was determined by titration at 65 °C with a standard solution of KMnO$_4$.

Results and discussion

The conventional ($\lambda = 1.5406$ Å) and synchrotron ($\lambda = 1.3271$ Å) powder XRD patterns of LiMn$_{2-x}$Co$_x$O$_4$ with $x = 0$ or 0.1 are shown in Fig. 1. Both compositions are of single phase. EDS measurements have shown that the ratio of Mn to Co in the composition with $x = 0.1$ is 95:5 which is consistent with the nominal composition. The peaks in each diffraction pattern can be indexed on the basis of a cubic unit cell (space group: Fd3m). The cell symmetry perovskite was identified by observation of the reflections with the limiting condition on hkl: h, k, l either all odd or all even, with F centering of the unit cell which is consistent with the results of the XRD pattern shown in Fig. 1. The observed and calculated diffraction profiles of the sample with $x = 0.1$ using conventional X-ray diffraction are shown in Fig. 2. The ideal crystal structure of LiMn$_{2-x}$Co$_x$O$_4$ with a cubic cell at room temperature is shown in the inset. The structural parameters of the LiMn$_{2-x}$Co$_x$O$_4$ compositions at room temperature are listed in Table 1. The lattice constant $a$ and Mn–Mn bond distances decrease with the addition of Co, which is due to the smaller size of the substituting Co$^{3+}$ ion [0.61 Å for C.N. (coordination number) = 6, in low field] as compared to the larger Mn$^{3+}$ ions (0.645 Å for C.N. = 6, in low field). The low temperature structure of LiMn$_{2-x}$O$_4$ was investigated by powder synchrotron diffraction. The data were collected using an image plate from 300 K to low temperatures. Fig. 3 shows the synchrotron powder diffraction profiles recorded from 300 to 25 K. Peak-broadening is clearly seen in the pattern.
at 220 K, especially for the peaks at high angles. The peaks at 11.17, 18.35, and 21.53° in 2θ are from grease (used to mount the sample on to the holder) and those at 33.13, 39.28 and 45.07° are from the beryllium sample holder.

*Fdd dawn* is a maximal non-isomorphic subgroup of *I4 1/amd* and derived from *Fd3m* by loss of all threefold rotation axes and part of the twofold screw axes. Wyckoff positions in the cubic spinel type structure, e.g. 8a (1/8, 1/8, 1/8), 16d (1/2, 1/2, 1/2) and 32e (x, x, x) sites in *Fd3m*, can be generated with symmetry operations in *Fddawn*. In *Fddawn* the corresponding Wyckoff positions are 8a (1/8, 1/8, 1/8), 16d (1/2, 1/2, 1/2) and 32h (x, y, z),

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<td>56.96</td>
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<td>56.69</td>
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Table 2 Comparison of calculated and observed peak positions for the space groups *Fd3m* and *Fddawn* of LiMnO4 with synchrotron wavelength 1.3271 Å.

Fig. 5 shows the diffraction patterns of LiMnO4 in the 46–59°(2θ) range at different temperatures from 300 to 25 K. With decreasing temperature, narrowing of the peaks is expected. However, the peaks become broader, as can be seen. From the patterns shown the (333) and (511) reflections around 2θ of 49.51° with the *Fd3m* cubic spinel split into (111) and (333) reflections of the orthorhombic *Fddawn* phase below 220 K. The (440) reflection at 54.23° splits into (440) and (404) reflections. The broadening of the (531) peak at 2θ 56.96° below 220 K is due to its splitting into four closely spaced reflections (531), (351), (315) and (153) as can be seen from Table 2. Yamaguchi et al. have used X-ray absorption spectroscopy of the manganese K edge to investigate the valence state and local structure of LiMnO4 at 280 K. The local structure was analyzed using isotropic Mn2+O4 and anisotropic Mn4+O4 octahedra in LiMn1+xO4. The structure exhibits local ordering of the distorted Mn2+O4 octahedra when the temperature is below the transition temperature. The macroscopic distortion appears by ordering the local Jahn–Teller distortion below the transition temperature of 220 K. Consequently, in the cubic phase above the transition temperature, the Mn2+O4 octahedra are distorted by the Jahn–Teller effect, which is a local distortion without static or dynamic order. Therefore, the charge ordering process is accompanied by the presence of an orbital ordering which is a manifestation of the Jahn–Teller polaronic nature of the mobile charge above and below the transition temperature.encia.

The chemical substitution of Co\(^{3+}\) for Mn\(^{3+}\) in LiMn\(_2\)O\(_4\) increases the valence of Mn. The valence in LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) as determined by chemical titration, is 3.526 ± 0.006. Therefore, the LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) composition can be written as Li(Co\(_{0.1}\)Mn\(_{1.9}\))O\(_4\). Shimakawa et al.\(^6\) have reported that in Li(Li\(_{0.06}\)Mn\(_{1.12}\))O\(_4\) and Li(Li\(_{0.06}\)Mn\(_{1.06}\))O\(_4\), the average manganese valence is greater than 3.5\(^{+}\) and the amount of the Jahn–Teller Mn\(^{3+}\) ions is less than 50\%. The samples with increased Li at the manganese site showed no anomalous change in resistivity and susceptibility. Yamada\(^8\) has observed that the DSC peaks corresponding to the phase transition were smeared out in Li(Li\(_{0.06}\)Mn\(_{1.06}\))O\(_4\). Fig. 6 shows the synchrotron diffraction patterns of LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) sample showing the cubic spinel peaks (333), (511), (440), and (531) in the 2θ range of 46–59° from 300 down to 25 K. As can be seen, there is no peak split or broadening from room to low temperature. Masquelier et al.\(^7\) have also reported that in the X-ray diffraction patterns of Li\(_{1-x}\)Co\(_{x}\)Mn\(_{2}\)O\(_4\), no peak splitting could be detected at 252, 298, and 103 K. In Li\(_{1-x}\)Co\(_{x}\)Mn\(_{1.9}\)O\(_4\), the Mn\(^{3+}\) content is reduced from 50\% (as in LiMn\(_2\)O\(_4\)) to 38\% for octahedral (16d) site in the [Mn\(_3\)O\(_6\)] spinel framework, which is sufficient to suppress the distortion at 103 K. The substitution effect of Co\(^{3+}\) on the framework would be local in the 16d site, which is similar to an excess of Li\(^{+}\) being substituted into the manganese site. In LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) the Mn\(^{3+}\) content decreases to 47\%, thus bringing about a change in the magnetic ordering. As we can see, the Mn\(^{3+}\) Jahn–Teller distortion is small in LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) at room temperature. However, at low temperature, the ordering of the distorted Mn\(^{3+}\)O\(_6\) octahedra is quite small in LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) as compared to the composition with LiMn\(_2\)O\(_4\).

In conclusion, we have carried out conventional and synchrotron powder X-ray diffraction studies of LiMn\(_{2-x}\)Co\(_x\)O\(_4\) with x = 0 and 0.1. LiMn\(_2\)O\(_4\) shows a phase transition at 220 K that is associated with cubic–orthorhombic distortion. Reduction of the concentration of the Mn\(^{3+}\) ions results in suppression of the Jahn–Teller distortion in LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) and the cubic phase is retained at low temperature.

**Acknowledgement**

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**References**


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**Fig. 6** Powder X-ray diffraction patterns of LiMn\(_{1.9}\)Co\(_{0.1}\)O\(_4\) at 2θ 46–59°, taken between 300 and 25 K with synchrotron wavelength 1.3271 Å.