

***Ab Initio* Structure Determination of Li_2MnO_3 from X-ray Powder Diffraction Data**V. MASSAROTTI,^a M. BINI,^a D. CAPSONI,^a A. ALTOMARE^b AND A. G. G. MOLITERNI^b^a*Dipartimento di Chimica Fisica dell'Università di Pavia e CSTE-CNR, Viale Taramelli 16, 27100 Pavia, Italy, and*^b*Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, CNR, c/o Dipartimento Geomineralogico, Campus Universitario, Via Orabona 4, 70125 Bari, Italy. E-mail: vimas@chifs.unipv.it*

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Abstract

The results of the structural determination of Li_2MnO_3 from X-ray powder diffraction data and the refinement by the Rietveld technique are presented. The Li_2MnO_3 structure has a monoclinic cell with space group $C2/m$ ($Z = 4$) and cell parameters $a = 4.9246$ (1), $b = 8.5216$ (1), $c = 5.0245$ (1) Å, $\beta = 109.398$ (1)°; the refinement with 14 structural parameters for 165 reflections in the pattern leads to $R_{wp} = 17.61\%$, $R_p = 13.25\%$, $R_B = 7.07\%$ and $S = 3.52$. Such a solution agrees with a single-crystal structure determination previously reported in the literature and allows other hypotheses to be rejected.

1. Introduction

In recent years, the system Li–Mn–O was largely investigated since some compounds such as LiMn_2O_4 and its derivatives obtained with Li-intercalation/deintercalation are used in the electrochemical field.

In a study of the spinel LiMn_2O_4 and its Li-rich phases $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ (Massarotti, Bini & Capsoni, 1996; Massarotti, Capsoni, Bini, Azzoni & Paleari, 1997) it was shown that, for lithium cationic fraction $x > 0.36$, the Li_2MnO_3 phase coexists with the spinel phases. To evaluate the spinel stoichiometry and phase abundance using the Rietveld refinement, a correct structural model of the coexisting compounds is required.

In the literature, several interpretations of the structure of Li_2MnO_3 are reported: cubic and hexagonal systems were proposed (Meyer & Hoppe, 1976) and more recent studies agree upon the monoclinic system but not upon the space group. A first work on X-ray powder diffraction data assigned the space group $C2/c$ to Li_2MnO_3 , according to the structure model of the isotype compound Li_2SnO_3 (Jansen & Hoppe, 1973). Recently, single-crystal diffraction studies proposed both space group $C2/c$ (Riou, Lecerf, Gerault & Cudennec, 1992) and $C2/m$ (Strobel & Lambert-Andron, 1988): in this last case the presence of a mirror

plane parallel to the ac plane was underlined that the other authors did not consider.

The aim of this work is to demonstrate that conventional laboratory X-ray powder diffraction data may very well be used for structure determination of compounds of low symmetry, like Li_2MnO_3 . For such a compound, a detailed comparison with the pertinent single-crystal data is possible. The programs actually available for the treatment of powder data are sufficiently reliable, and represent a valid choice when single-crystal data cannot be obtained. Many different programs were used in each step for the *ab initio* structure determination, both to test the solution found and to compare different computing methods.

2. Experimental**2.1. Products**

The Li_2MnO_3 compound was synthesized from the reacting mixture $\text{MnO}/\text{Li}_2\text{CO}_3$ with lithium cationic fraction $x = 0.667$. This mixture was heated in air up to 1173 K and, after an isothermal step of 20 h, it was cooled to room temperature (heating and cooling rate 5 K min^{-1}).

2.2. Apparatus and procedure

Diffraction data were obtained on a Philips PW 1710 powder diffractometer equipped with a Philips PW 1050 vertical goniometer with a radius of 173 mm.* The $\text{Cu K}\alpha$ radiation ($K\alpha_1 = 1.5406$, $K\alpha_2 = 1.5443$ Å) was selected by means of a graphite monochromator. A system of diverging, receiving and anti-scattering slits of 1, 0.2 and 1°, respectively, was used; two Soller slits were positioned both on the incident beam, before the divergent slit, and on the diffracted beam before the monochromator.

*The numbered intensity of each measured point on the profiles has been deposited with the IUCr (Reference: VI0070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Cell constants reported in the literature and evaluated by *ITO* and *TREOR* (with pertinent figures of merit and number of theoretical lines N_n)

FOM₂₀ is the figure of merit given by *ITO*. The meanings of M_n and F_n are the same as defined by de Wolff (1968) and Smith & Snyder (1979), respectively.

| | a (Å) | b (Å) | c (Å) | β (°) | Figure of merit |
|---------------------------------|---------|---------|---------|-------------|--|
| <i>ITO</i> solution <i>A</i> | 4.9219 | 8.5164 | 5.0249 | 109.3861 | FOM ₂₀ = 95.1 |
| <i>ITO</i> solution <i>B</i> | 4.9224 | 8.5155 | 9.6069 | 99.5179 | FOM ₂₀ = 36.1 |
| <i>TREOR</i> solution <i>A</i> | 4.9283 | 8.5253 | 5.0281 | 109.40 | $F_{24} = 25, M_{24} = 27; N_{24} = 81$ $F_{20} = 34, M_{20} = 37; N_{20} = 52$ |
| <i>TREOR</i> solution <i>B</i> | 5.0282 | 8.5251 | 9.4607 | 100.68 | $F_{24} = 13, M_{24} = 14; N_{24} = 160$ $F_{20} = 17, M_{20} = 18; N_{20} = 104$ |
| Jansen & Hoppe (1973) | 4.92 | 8.53 | 9.60 | 99.5 | |
| Riou <i>et al.</i> (1992) | 4.921 | 8.526 | 9.606 | 99.47 | |
| Strobel & Lambert-Andron (1988) | 4.937 | 8.532 | 5.030 | 109.46 | |

The pattern was collected with 40 kV of tube voltage and 35 mA of tube current in the angular range $15 < 2\theta < 115^\circ$ in step scan mode (step width 0.02° , counting time 10 s step^{-1}).

In some stages of Li_2MnO_3 *ab initio* structure determination, different programs were used to check the reproducibility of the results. For example, *ITO* (Visser, 1969) and *TREOR* (Werner, Eriksson & Westdahl, 1985) were used for the automatic indexing procedure, while *ALLHKL* (Pawley, 1981) and *EXTRA* (Altomare *et al.*, 1995) were used for the full-profile peak decomposition and extraction of the square structure-factor moduli ($|F|^2$). The determination of the atomic positions of the structure was obtained by the direct-methods program *SIRPOW.92* (Altomare *et al.*, 1994), then the profile refinement, by the Rietveld method, was performed using *DBWS* (Wiles & Young, 1981) and *WYRIET 3.5* (Schneider, 1989).

3. Results

3.1. Indexing

To obtain precise peak positions, the profile-fitting program available in the Philips APD software was used. A set of the first 24 experimental diffraction peaks was used for the automatic indexing with programs *ITO* and *TREOR* that were tested with different values of the available options to verify the reproducibility of the results. Two monoclinic solutions, *A* and *B*, whose figures of merit and cell constants are reported in Table 1, were found by *ITO* with a twotheta-zero correction of 0.02° (value comparable with that usually measured with our instrumentation) and without correction, respectively. The same results are also proposed by *TREOR* (see Table 1): in this case, the *A* or *B* solutions are achieved depending on the value selected for the option 'maximum cell volume' (250 or 500 Å^3 , respectively). The cell constants agree quite well with those reported in the literature (see Table 1): the figures of merit are significantly higher for *A* according to the lower number of theoretical lines of this case with

respect to the pertinent number for *B* (in Table 1 the number of theoretical lines is also reported). The *A* solution can explain all the observed lines with the minimum cell volume and has been selected for the determination of the space group.

In Table 2, the experimental 2θ peak positions are reported and compared with those calculated with *ITO* and *TREOR*; the Miller indices are also reported. The systematic absences (hkl : $h + k = 2n + 1$; $h0l$ and $00l$: no conditions for l) are consistent only with the space groups *C2*, *Cm* and *C2/m*.

3.2. Extraction of the structure-factor moduli

The full-profile fitting and peak decomposition were performed in the angular range $15 < 2\theta < 110^\circ$ with the two programs *ALLHKL* and *EXTRA* using the pseudo-Voigt and PearsonVII profile function, respectively: the $|F|^2$ set was extracted and the profile parameters and cell constants were refined.

There is a satisfactory agreement between the results found with the two programs. The discrepancy factors obtained with *ALLHKL* are $R_{wp} = 25.5\%$ and $R_p = 17.0\%$, while with *EXTRA* $R_{wp} = 29.90\%$ and $R_p = 18.25\%$ were obtained. As an example, Figs. 1(a) and 1(b) show the comparison between the observed and calculated pattern obtained after the full-profile fitting performed with *ALLHKL* and *EXTRA*, respectively.

3.3. Structure determination

The *SIRPOW.92* program was applied both to the $|F|^2$ set extracted by *ALLHKL* and by *EXTRA*, using the space group *C2/m*: independently of the set of $|F|^2$ used for the structure determination, the same literature solution (Strobel & Lambert-Andron, 1988) was obtained, apart from a shift of the cell origin to $\frac{1}{2}, 0, 0$. The atomic positions and occupancies determined with *SIRPOW.92*, the Fourier peak heights and the discrepancy factors obtained after the Fourier least-squares procedure are reported in Table 3; for comparison, the literature atomic positions (Strobel & Lambert-Andron,

Table 2. Comparisons between the experimental and calculated 2θ position (ITO and TREOR) and Miller indices

| 2θ Experimental | 2θ ITO | 2θ TREOR | hkl | 2θ Experimental | 2θ ITO | 2θ TREOR | hkl |
|------------------------|---------------|-----------------|-------------|------------------------|---------------|-----------------|-------------|
| 18.678 | 18.68 | 18.695 | 001 | 49.694 | 49.72 | 49.683 | $22\bar{2}$ |
| 20.794 | 20.82 | 20.822 | 020 | | 49.76 | 49.747 | 112 |
| 21.734 | 21.76 | 21.759 | 110 | 53.805 | 53.83 | 53.793 | 221 |
| 24.213 | 24.26 | 24.251 | $11\bar{1}$ | 55.849 | 55.88 | 55.862 | $11\bar{3}$ |
| 28.102 | 28.12 | 28.124 | 021 | | 57.11 | | $31\bar{1}$ |
| 32.831 | 32.84 | 32.837 | 111 | | 57.51 | 57.463 | $24\bar{1}$ |
| 36.984 | 36.98 | 36.957 | $20\bar{1}$ | 57.509 | 57.57 | 57.528 | 150 |
| 37.045 | 37.07 | 37.048 | 130 | | 58.18 | | 042 |
| 37.886 | 37.89 | 37.886 | $11\bar{2}$ | | 58.33 | | 003 |
| | 37.91 | 37.913 | 002 | | 58.70 | 58.664 | $20\bar{3}$ |
| 38.653 | 38.65 | 38.636 | $13\bar{1}$ | 58.694 | 58.72 | 58.675 | $15\bar{1}$ |
| | 38.74 | 38.711 | 200 | | 58.78 | 58.730 | 240 |
| 42.373 | 42.40 | 42.374 | 040 | 58.962 | 58.99 | 58.967 | 132 |
| 42.786 | 42.83 | 42.796 | $22\bar{1}$ | | 60.53 | | $31\bar{2}$ |
| 43.650 | 43.65 | 43.645 | 022 | | 60.76 | | 310 |
| | 44.39 | | 220 | | 62.64 | | 023 |
| 44.584 | 44.60 | 44.575 | $20\bar{2}$ | | 62.99 | | $22\bar{3}$ |
| 44.788 | 44.82 | 44.798 | 131 | | 63.24 | | $24\bar{2}$ |
| 46.699 | 46.71 | 46.686 | 041 | | 63.41 | | 151 |
| 48.810 | 48.83 | 48.806 | $13\bar{2}$ | 64.509 | 64.53 | 64.497 | $13\bar{3}$ |
| | 49.03 | | 201 | | | | |

1988) and the Wyckoff's symbols (*International Tables for X-ray Crystallography*, 1974) are also shown. The atomic positions found by *SIRPOW.92* with $|F|^2$ set by *ALLHKL* are obtained using the directive 'pseudo' in the normalization process to actively use the pseudo-

translational symmetry information estimated by the program itself. The atomic positions found by *SIRPOW.92* with $|F|^2$ set by *EXTRA* are obtained in a default way.

Regarding the *SIRPOW.92* application (set of $|F|^2$ by *ALLHKL* and *EXTRA*) to the space groups *C2* and *Cm*, which have the same systematic absences as *C2/m*, the cell content determined disagrees with the stoichiometry of Li_2MnO_3 . On the other hand, these two space groups were already rejected on the basis of piezoelectric behaviour (Strobel & Lambert-Andron, 1988).

3.4. Structure refinement

The structure data obtained in the previous step with space group *C2/m* were used as starting parameters in the model for the Rietveld profile refinement with *WYRIET*. The structural and profile parameters, according to the profile function PearsonVII, were evaluated with the procedure using the following order of variation: (i) scale factor, twotheta-zero correction and one background coefficient; (ii) cell parameters; (iii) three background coefficients; (iv) profile parameters; (v) atomic positions and isotropic thermal factors (the atomic coordinates were fixed before the next step); (vi) site occupancies. In each step, the parameters varied were added to the previous ones: 24 parameters were refined in the last stage.

In Table 4 the values obtained for the refined parameters (atomic positions, isotropic displacement factors, occupancies and cell constants) and the discrepancy factors are reported. The comparison between the observed and calculated pattern and the difference curve is shown in Fig. 2 and the content of the unit cell is represented in Fig. 3.

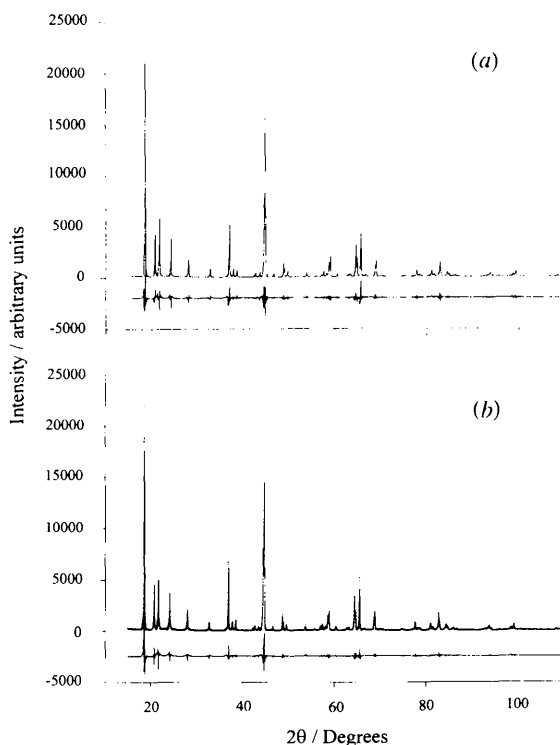


Fig. 1. Comparison between observed (dots) and calculated (solid line) X-ray patterns after the fitting process by programs (a) *EXTRA*, and (b) *ALLHKL*. In the lower part of each pattern fit, the difference curve is plotted.

Table 3. Fourier peak heights, atomic positions and occupancies obtained by *SIRPOW* from two different sets of $|F|^2$ (*EXTRA* and *ALLHKL*) compared with the literature solution (Strobel & Lambert-Andron, 1988)

SIRPOW solution: $R_F = 10.45\%$ ($|F|^2$ extracted with *EXTRA*)

| Atom | Peak height | x | y | z | Occupancy |
|------|-------------|-------|-------|-------|-----------|
| Mn | 4908 | 0.0 | 0.333 | 0.0 | 0.5 |
| O | 1939 | 0.241 | 0.326 | 0.774 | 1.0 |
| O | 1869 | 0.235 | 0.5 | 0.233 | 0.5 |
| Li1 | 1634 | 0.5 | 0.5 | 0.0 | 0.25 |
| Li3 | 871 | 0.0 | 0.170 | 0.5 | 0.5 |
| Li2 | 368 | 0.0 | 0.5 | 0.5 | 0.25 |

SIRPOW solution: $R_F = 7.95\%$ ($|F|^2$ extracted with *ALLHKL*)

| Atom | Peak height | x | y | z | Occupancy |
|------|-------------|-------|-------|-------|-----------|
| Mn | 4715 | 0.0 | 0.331 | 0.0 | 0.5 |
| O | 1483 | 0.252 | 0.325 | 0.780 | 1.0 |
| O | 1237 | 0.224 | 0.5 | 0.235 | 0.5 |
| Li1 | 919 | 0.5 | 0.5 | 0.0 | 0.25 |
| Li3 | 545 | 0.0 | 0.177 | 0.5 | 0.5 |
| Li2 | 456 | 0.0 | 0.5 | 0.5 | 0.25 |

Literature solution

| Atom | Wyckoff symbol | x | y | z |
|------|----------------|-------|-------|-------|
| Mn | 4g | 0.5 | 0.333 | 0.0 |
| O1 | 8j | 0.746 | 0.321 | 0.777 |
| O2 | 4i | 0.719 | 0.5 | 0.227 |
| Li1 | 2b | 0.0 | 0.5 | 0.0 |
| Li3 | 4h | 0.5 | 0.161 | 0.5 |
| Li2 | 2c | 0.5 | 0.5 | 0.5 |

4. Discussion

The comparison between the single-crystal and powder-crystal structure results has clearly shown the possibility of indexing the powder pattern and solving the structure by direct methods.

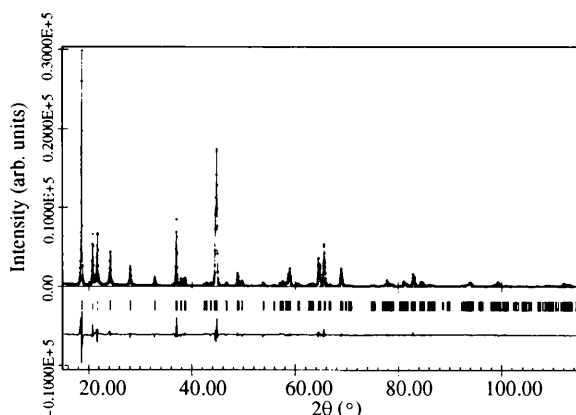


Fig. 2. Comparison between observed (dots) and calculated (solid line) X-ray patterns after Rietveld refinement. In the lower part the difference curve is plotted and bars for the reflection positions are shown.

In the indexing process the equivalence of the results proposed by programs *TREOR* and *ITO* can be seen; the latter calculates a complete list of hkl (see Table 2), nevertheless *TREOR* indexing allows the systematic absences and the symmetry of the compound to be unequivocally estimated. Moreover, it can be noted that, already in this indexing step, the ambiguity about the monoclinic space group to which Li_2MnO_3 belongs [$C2/m$ (*A*) or $C2/c$ (*B*)] is clarified and the pertinent figures of merit (see Table 1) allow the *B* solution to be rejected, for which many additional reflections were calculated, some of which having appreciable intensity (e.g. 021 and 02 $\bar{1}$ reflections at $2\theta = 22.86^\circ$) in angular regions where no reflection was observed.

As previously discussed in §3.2, the programs *ALLHKL* and *EXTRA* give comparable results in the peak decomposition and in the evaluation of the integrated intensities set. However, it can be underlined that the *EXTRA* program is really user friendly and more complete than *ALLHKL*: it can operate with all space groups. Moreover, previous data treatment (e.g. $K\alpha_2$ stripping, background evaluation and profile parameters estimates) can be automatically performed by *EXTRA*.

Regarding the atomic positions search, it can be noted (see Table 3) that the solution agrees remarkably well with the single-crystal results, and the obtained values of R_F are satisfactory.

The structure parameters refinement with the Rietveld method starting from the atomic positions obtained by *SIRPOW.92* led to values very close to the pertinent single-crystal data (Strobel & Lambert-Andron, 1988) (see Table 4). Regarding the isotropic thermal factor values, only for Li1 site was a negative value of B found. This anomalous behaviour of the Li1 atom has already been reported from both single-crystal and neutron powder data studies (Strobel & Lambert-Andron, 1988). For a better determination of the B value for the Li1 site it was made possible to increase its electron density by considering variable occupation factors of Li and Mn on

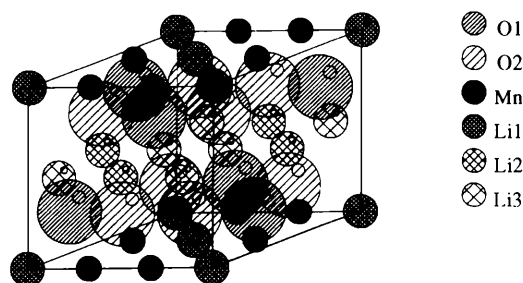


Fig. 3. Li_2MnO_3 unit-cell plot after Rietveld refinement.

Table 4. Structural parameters, cell constants and discrepancy factors obtained using the Rietveld method

| Atom | x | y | z | B_{iso} (\AA^2) | Occupancy |
|-------|-------------|-------------|------------|------------------------------|-----------|
| Mn1 | 0.0 | 0.3323 (2) | 0.0 | 0.83 (4) | 0.5 |
| O1 | 0.2205 (11) | 0.5 | 0.2291 (8) | 0.01 (10) | 0.5 |
| O2 | 0.2409 (9) | 0.3175 (4) | 0.7747 (6) | 0.63 (8) | 1.0 |
| Li1 | 0.5 | 0.5 | 0.0 | -3.1 (3) | 0.245 (1) |
| Mn1s* | 0.5 | 0.5 | 0.0 | -3.1 (3) | 0.005 (1) |
| Li2 | 0.0 | 0.5 | 0.5 | 1.5 (4) | 0.25 |
| Li3 | 0.0 | 0.1660 (20) | 0.5 | 2.0 (3) | 0.5 |

Cell parameters: $a = 4.9246$ (1) \AA , $b = 8.5216$ (1) \AA , $c = 5.0245$ (1) \AA , $\beta = 109.398$ (1) $^\circ$

R values (%): $R_p^\dagger = 13.25$, $R_{wp}^\ddagger = 17.61$, $S^\S = 3.52$, $D^\P = 0.27$, $R_B^{**} = 7.07$

* Substitutional Mn on Li1 site. † Profile discrepancy factor. ‡ Weighted profile discrepancy factor. § Goodness of fit. ¶ Weighted Durbin–Watson statistic d . ** Bragg discrepancy factor. The meanings of the above discrepancy factors are reported in Wiles & Young (1981).

the site, according to the fact that the Fourier peak height for Li1 is sensibly higher than the ones of the other Li atoms (see Table 3). Nevertheless, the quantity of substitutional Mn, independently from its initial value, reaches a refined content lower than that found by Strobel & Lambert-Andron (1988) in samples synthesized by solid-state reaction. The simultaneous variation of temperature and occupation factors shows a correlation factor of $\sim 70\%$ and the refined values may be believed as reliable. Notwithstanding the presence of substitutional defect, the isotropic thermal factor remained negative and no other correction was made.

The Rietveld procedure, performed on the basis of 14 structural parameters for 165 reflections in the pattern, gave a rather high goodness-of-fit value. However, the structural results can be considered in good agreement with the literature (Table 3 and 4). The discrepancy factors are also reported in Table 4. In Fig. 2 the comparison between observed and calculated patterns is shown. It may be observed that some inadequacy of the profile causes the underestimation of the calculated intensity for certain reflections: this may be attributed to the presence of microstructural effects as previously reported by Massarotti, Capsoni, Bini, Azzoni & Paleari (1997). A more complete analysis of the influence of crystallite size and microstrain on the peak shape of the Li_2MnO_3 phase will be the object of a further study.

Finally, in spite of lower precision usually attributed to data collected from conventional X-ray powder diffractometers, the structure of Li_2MnO_3 was determined and the results agree with single-crystal data. It is also shown that presently available programs for treating powder X-ray diffraction data allow the *ab initio*

structure determination even for low-symmetry crystalline compounds.

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