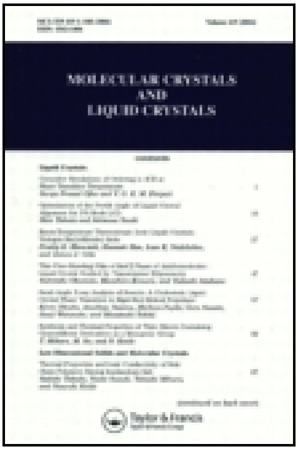

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 27 Oct 2006

To cite this article: Fujio Izumi, Takuji Ikeda, Takayoshi Sasaki & Shintaro Kumazawa (2000): Disordered Distribution of K^+ Ions Interlayered in $K_xTi_{2-x/3}Li_{x/3}O_4(x = 0.8)$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 253-258

To link to this article: http://dx.doi.org/10.1080/10587250008026149

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 253-258
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Disordered Distribution of K^+ Ions Interlayered in $K_xTi_{2-x/3}Li_{x/3}O_4 (x = 0.8)$

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(In final form June 28, 1999)

An integrated software system, REMEDY, has been developed for MEMbased whole-pattern fitting. REMEDY was applied to the determination of the crystal structure and electron densities for $K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.8$). We have successfully revealed the positional disorder of K^+ ions between $Ti_{2-x/3}Li_{x/3}O_4$ layers consisting of edge-sharing $(Ti,Li)O_6$ octahedra. Possible incorporation of residual water molecules is also suggested.

Keywords: X-ray powder diffraction; Rietveld method; maximum-entropy method; whole-pattern fitting; positional disorder; electron density

INTRODUCTION

$K_xTi_{2-x/3}Li_{x/3}O_4$[1,2] belongs to a family of layered compounds with a general formula $A_xTi_{2-y}M_yO_4$ (A = K, Rb, and Cs; M = Li, Mg, Mn(III), Fe(III), Co, Ni, Cu, and Zn)[3]. Sasaki *et al.*[2] studied the structures, protonic forms, and ion-exchange/intercalation properties of $A_xTi_{2-x/3}Li_{x/3}O_4$. These oxides contain lepidocrocite-related $Ti_{2-x/3}Li_{x/3}O_4$ layers composed of edge-sharing $(Ti,Li)O_6$ octahedra and charge-balancing K^+ ions in the interlayer domain. Rietveld refinement of $K_xTi_{2-x/3}Li_{x/3}O_4$ with neutron powder diffraction data showed K^+ ions to be highly disordered between two $Ti_{2-x/3}Li_{x/3}O_4$ layers; an apparently large isotropic atomic displacement parameter, B, of 10 Å^2 for K evidently reflects its positional disorder. In other words, the real structure is not fully expressed with the conventional Rietveld analysis, where structure factors are calculated from structure parameters such as fractional coordinates. The present work was undertaken to obtain more detailed information about the disordered configuration of K^+ ions and interstitial defects in $K_xTi_{2-x/3}Li_{x/3}O_4$ with a more advanced and elaborate technique of structure refinement.

REFINEMENT PROCEDURES

A Rietveld-analysis program RIETAN-98[4] has recently been combined with a MEED program[5] for a maximum-entropy method (MEM) to be integrated into a system named REMEDY[6]. Figure 1 illustrates the flow chart of Rietveld analysis followed by alternate MEM analyses and whole-

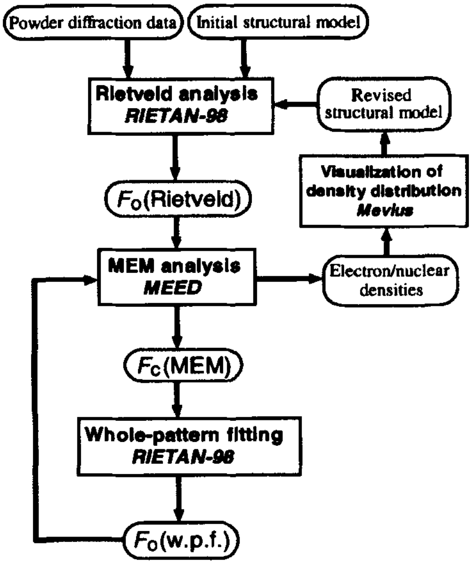

FIGURE 1 A sequence of structure refinement by Rietveld analysis and MEM-based whole-pattern fitting.

pattern fitting (w.p.f.). After Rietveld analysis, 'observed' structure factors, F_o(Rietveld)'s, are evaluated by partitioning observed intensities among overlapping reflections in proportion to their profiles calculated from final parameters in Rietveld analysis. The F_o(Rietveld)'s are analyzed by the MEM to give three-dimensional electron or nuclear densities, which are more or less biased by a structural model in Rietveld analysis. We can, however, extract structural details from the F_o(Rietveld)'s by the MEM because they contain contributions that have not been introduced into the structural model. Such visualization of diffraction data by the MEM is very useful for modifying imperfect structural models[7,8] but far from perfect for determining accurate electron/nuclear densities.

MEED evaluates structure factors, F_c(MEM)'s, by the Fourier transform of three-dimensional electron/nuclear densities. Then, we can fit the powder pattern calculated from the F_c(MEM)'s to the whole observed one to refine parameters other than structure parameters. F_o(w.p.f.)'s estimated after the whole-pattern fitting according to the procedure described above are analyzed again by the MEM. MEM analysis and whole-pattern fitting are alternately repeated in such a manner until R factors in the pattern fitting no longer decrease. The influence of the structural model on F_o(w.p.f.)'s diminishes with increasing number of iterations. This iterative method[6] is capable of modeling disordered atomic arrangements, covalent bondings, nonlocalized electrons, and anharmonic thermal motion more adequately than the conventional Rietveld method.

RESULTS AND DISCUSSION

$K_xTi_{2-x/3}Li_{x/3}O_4$ ($x = 0.8$) was prepared by solid-state reaction according to a procedure reported previously[2]. Its X-ray powder diffraction pattern was measured at room temperature in vacuo with CuKα radiation on a MAC Science MXP 3TZ diffractometer equipped with a pair of long Soller slits to decrease the angular aperture to 1°[9].

The X-ray intensity data were analyzed by the Rietveld method on the basis of our previous structural model with space group Cmcm (No. 63)[2]. A split-type pseudo-Voigt function was used as a profile function with its modified function applied to part of reflections for partial profile relaxation[4,6] to improve fits for these reflections broadened anisotropically. Background

TABLE I Structure parameters determined by the Rietveld refinement of $K_{0.8}Ti_{1.733}Li_{0.267}O_4$ (Z = 2). a = 3.82484(6) Å, b = 15.5439(5) Å, c = 2.97370(8) Å, and V = 176.795(8) Å^3.

Atom	Site	x	y	z	g	B/Å^2
K	4c	0	0.0080(4)	1/4	0.4	5.53(13)
Ti/Li	4c	0	0.68637(8)	1/4	0.867/0.133	1.09(2)
O1	4c	0	0.2159(2)	1/4	1	1.21(8)
O2	4c	0	0.3874(2)	1/4	1	2.78(10)
O3	8f	0	0.076(4)	0.02(2)	0.028(3)	1

intensities were evaluated by interpolating smoothed intensities at specified 2θ's where contributions of Bragg reflections were regarded as negligible.

Preliminary Rietveld analysis showed B(K) to be extraordinarily large, which suggests that K^+ ions are disordered to a greater extent than in the structural model. Determination of electron densities with REMEDY was expected to make it possible to visualize how K^+ ions are distributed in between $Ti_{2-x/3}Li_{x/3}O_4$ layers. Then, we carried out MEM analysis of F_o(Rietveld)'s, with an unexpected result that low peaks were detected at an 8f site (0, y, z; $y \approx 0.08$ and $z \approx 0.02$) near the K site in an electron-density map. These positions may be slightly occupied not by oxide ions but by oxygen atoms in residual water molecules in view of the achievement of electrical neutrality. We therefore added site O3 in the final Rietveld analysis and refined its occupancy, g, with fixing its B arbitrarily at 1 Å^2.

Table I lists the resulting structure parameters with estimated standard deviations of the last significant digit in parentheses. R factors were R_{wp} = 11.56% (R_e = 10.54%), R_p = 8.41%, R_B = 5.35%, and R_F = 4.38%. A chemical composition of $K_{0.8}Ti_{1.733}Li_{0.267}O_4 \cdot 0.112H_2O$ is obtained from g(O3) provided that residual water is really interlayered.

Subsequent three iterations of MEM analyses and whole-pattern fitting lowered all the R factors: R_{wp} = 10.63%, R_p = 7.65%, R_B = 1.53%, and R_F = 1.16%. The improvements of R_B and R_F are very pronounced, reflecting better representation of the detailed structure by calculating structure factors from electron densities than from structure parameters in Rietveld analysis. Figure 2 shows observed (plus symbols), calculated (higher solid line), and difference (lower solid line) patterns plotted after the final whole-pattern fitting. The very excellent fit was evidently achieved not only by

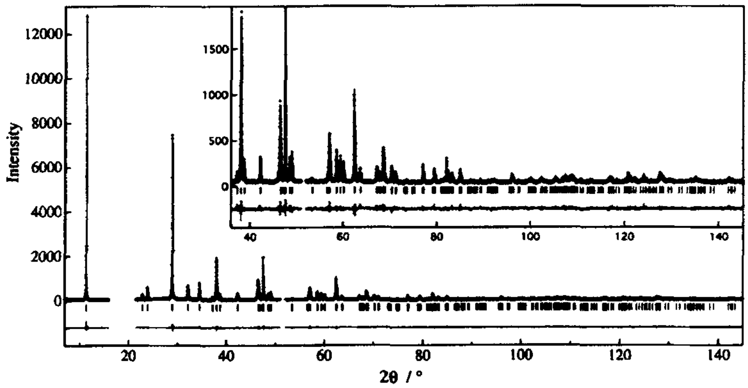

FIGURE 2 Whole-pattern fitting for $K_{0.8}Ti_{1.733}Li_{0.267}O_4$. The inset shows magnified patterns from 36° to 145°.

the satisfactory modeling of the disordered and defect structure but also by partial profile relaxation[4].

Figure 3 displays a final electron-density map determined for the (100) plane. Neither negative densities nor distinct ripples appeared at all, which is a great advantage of the MEM over Fourier synthesis. A stream of K^+ ions along the [001] direction was clearly visualized by virtue of those iterative analyses by the MEM and whole-pattern fitting which have been first applied to a study of spatial distribution for highly disordered chemical species. The winding of the cationic stream is ascribed to the attraction of K^+ ions to O1 atoms in $(Ti,Li)O_6$ octahedra. Positional disordering of K^+ ions must arise from large differences in the oxidation states and effective ionic radii[10], r, of Ti^{4+} (r = 0.605 Å) and Li^+ (r = 0.76 Å) ions sharing the same octahedral site.

CONCLUDING REMARKS

We have verified that REMEDY is available for clarifying the positional disorder of K^+ ions which cannot be adequately represented in conventional Rietveld analysis. In addition, we detected a minute amount of residual water whose occupancy is as low as 0.028, which led us to modify the in-

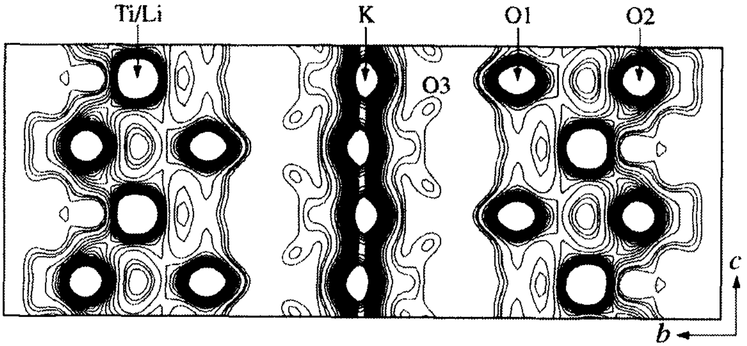

FIGURE 3 Electron-density distribution determined for the (100) section of $K_{0.8}Ti_{1.733}Li_{0.267}O_4$. Range: 0.2–8 e/Å^3.

complete structural model, *i.e.*, add the interstitial O3 site. REMEDY is expected to be effective for intercalation and clathrate compounds where guests are disordered to such an extent that the so-called split-atom model fails in giving reasonable atomic displacement parameters or sufficiently low *R* factors. We shall apply REMEDY to a variety of compounds whose structures cannot be represented satisfactorily with structure parameters.

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