JOURNAL OF SOLID STATE CHEMISTRY **78**, 170–177 (1989)

Refinement of the Lithium Distribution in $Li_2Ti_3O_7$ Using High-Resolution Powder Neutron Diffraction

I. ABRAHAMS AND P. G. BRUCE*

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, Scotland, United Kingdom

W. I. F. DAVID

Neutron Division, Rutherford-Appleton Laboratory, SERC, Chilton, Didcot, Oxon OX11 OQX, United Kingdom

AND A. R. WEST

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland, United Kingdom

Received May 18, 1988; in revised form September 8, 1988

The crystal structure of lithium titanate ($Li_2Ti_3O_7$) has been refined from high-resolution time-of-flight powder neutron diffraction data using a modified Rietveld method; this has permitted a more precise determination of the lithium ion distribution than previous X-ray work. The structure is ramsdellite-like. Some of the lithium and all of the titanium atoms are disordered over the octahedral sites of the framework. The remaining lithiums partially occupy distorted tetrahedral sites in the open channels. The structure was solved in the orthorhombic space group *Pnma*, and has eight oxygen atoms per unit cell giving a unit cell formula $Li_{2.29}Ti_{3.43}O_8$ with $Z = 1$ and $D_c = 3.64$ g cm^{-3}. The refined cell parameters are $a = 9.5423(1)$, $b = 2.9438(1)$, and $c = 5.0136(1)$ Å with $R_{wp} = 8.06\%$, $R_{ex} = 6.40\%$, for 41 basic variables.

Introduction

In the search for fast ion conducting solid electrolytes a range of diverse materials have been examined. The lithium ion conducting solid solutions such as LISICON ($Li_{(2+2x)}Zn_{(1-x)}GeO_4$) (*1, 2*) have received particular attention because the electropositive nature of lithium combined with its light weight make it an attractive material for battery applications. Several lithium titanates have been prepared including Li_4TiO_4 (*3*), Li_2TiO_3 (*4*), and $Li_2Ti_3O_7$ (*5, 6*), and their conductivities have been measured, the latter being the subject of this paper. $Li_2Ti_3O_7$ crystallizes with the ramsdellite (γ-MnO_2) structure which belongs to the class of framework structure types. Its structure consists of distorted MO_6 octahedra which link up with adjacent octahedra, by sharing opposite edges, to form columns. Pairs of adjacent columns share

---

* To whom correspondence should be addressed.

0022-4596/89 $3.00

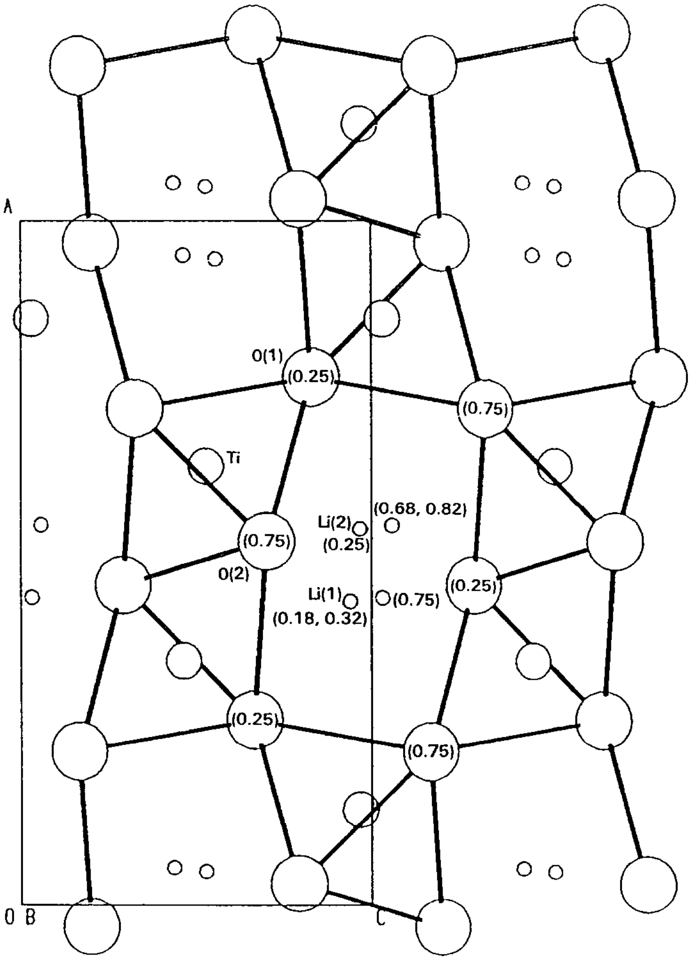

FIG. 1. Projection onto *a*/*c* cell plane of $Li_2Ti_3O_7$ with heights along *b*-axis given.

edges to form double columns (Fig. 1), giving rise to an open structural framework. In between the double columns are channels running parallel to the columns that contain distorted interstitial sites. Since there are eight oxygens in the orthorhombic unit cell, the formula of $Li_2Ti_3O_7$ is more usefully written as $Li_{2.29}Ti_{3.43}O_8$. X-ray crystallographic studies (*7*) have unambiguously located the titanium and oxygen positions in the structural framework. The exact lithium distribution is however still in question. In (*7*), Morosin and Mikkelsen suggested two extreme models for the lithium ion distribution in this material; in model I all the lithium ions are located in the channels, c, leaving 0.57 vacancies per cell on the cation sites in the framework, f, i.e., $(Li_{2.29})_c(Ti_{3.43}[\ ]_{0.57})_fO_8$; in model II the framework cation sites are fully occupied by Ti and Li $((Li_{1.72})_c(Ti_{3.43}Li_{0.57})_f(O_8)$. These workers were unable to refine the lithium ion distribution between channel and framework sites although their *R*-factors indicated a minimal but inconclusive preference for model II. Compared with Ti and O, Li is a weak scatterer of X-rays; however, ^7Li scatters neutrons strongly.

For this reason we chose to determine the structure of $Li_2Ti_3O_7$ by powder neutron diffraction in order to obtain a more accurate lithium ion distribution.

Experimental

Preparation

$Li_2Ti_3O_7$ was prepared by solid-state reaction between $^7Li_2CO_3$ and TiO_2, as described previously (*6*).

Data Collection

A high-resolution time-of-flight (t.o.f.) powder neutron diffraction profile was collected on the HRPD diffractometer at ISIS, Rutherford-Appleton Laboratory. This instrument possesses a theoretical resolution $\Delta d/d$ of 5×10^{-4} and a range of *d*-spacings from 0.4 to 6 Å may be examined. Two sample positions are possible, at 1 and 2 m in front of banks of backscattering detectors. Approximately 10 g of powdered $Li_2Ti_3O_7$ was placed in a vanadium sample can and data collected in the t.o.f. range $20–120 \times 10^3$ μs in the 2-m sample position. The data were fitted using a modified Rietveld method with the peak shape modeled by a convolution of Gaussian and exponential functions. The scattering lengths used were $Ti = -0.3438$, $O = 0.5805$, $^7Li = -0.220 \times 10^{-12}$ cm (*8*).

Structure Determination

The structure of $Li_2Ti_3O_7$ was determined in the orthorhombic space group *Pnma* (No. 62 (*9*)) with initial cell dimensions determined by refinement of *d*-spacings from the X-ray powder diffraction pattern of this material. Although the profile was satisfactorily indexed on the orthorhombic ramsdellite cell, close examination of the profile revealed a very small amount of additional scattering which appeared as shoulders on the low time-of-flight (low *d*-spacing) side of several of the peaks; however, 0*k*0 peaks did not show these shoulders. These additional peaks could not be indexed on the same orthorhombic unit cell as the major peaks. Instrumental factors were eliminated as the origin of the additional scattering by examination of profiles of similar materials collected under identical conditions. The possibility that the additional peaks signaled a lowering of symmetry from *Pnma* was considered. Reflections such as 3 0 2 and 1 1 2 were evidently split whereas those such as 0 2 0 were not; this could be indicative of monoclinic symmetry. The observed absences are consistent with space group $P2_1/m$; however, attempts to refine the structure in this space group consistently resulted in a β angle of 90°. It appeared that the entire pattern could probably not be indexed on one unit cell and that the primary peaks were correctly assigned to *Pnma*. The additional peaks did not match those calculated for any of the likely impurities or known lithium titanate phases. The extra peaks could, however, be indexed on a new orthorhombic unit cell, space group *Pnma*. A monoclinic cell would also fit the data, the quality of which was too low to discriminate between the two cells. We did not feel justified in choosing the lower symmetry cell. We concluded that the shoulders resulted from the presence in the powder of a ramsdellite phase with a different composition to that of the primary phase. The cell dimensions of the secondary phase refined to yield *a* and *c* lattice parameters of 9.522 and 5.004 Å, respectively, which are smaller than those of the primary phase but a *b* parameter of 2.945 Å which is very similar to that of the primary phase. A powder profile was calculated for the second phase using the refined cell dimensions and the crystal structure data of Morosin and Mikkelsen (*7*). This was used to subtract the scattering due to the second phase from the overall profile. A package for multipattern refinement of ISIS

TABLE I

TRIAL Li POSITIONS IN $Li_2Ti_3O_7$

Position	Label	Wyck.	x/a	y/b	z/c
Reg. Tet.	B1	4c	0.45	0.25	0.60
Reg. Tet.	B2	4c	0.30	0.25	0.31
Dist. Oct.	A1	4c	0.63	0.25	0.04
Dist. Oct.	A2	4c	0.38	0.25	−0.04
Dist. Tet.	D	8d	0.63	0.00	0.04
Dist. Tet.	C1	4c	0.59	0.25	−0.05
Dist. Tet.	C2	4c	0.66	0.25	0.14
Dist. Tet.	C3	4c	0.33	0.25	0.03
Dist. Tet.	C4	4c	0.42	0.25	−0.11

data is not presently available and it is doubtful whether the very small additional scattering due to the second phase could be refined satisfactorily.

The starting model for refinement of the corrected profile was based on the structure reported by Morosin and Mikkelsen (*7*). In the initial refinement only the titanium and oxygen positions were included. The scale and zero point parameters were refined first followed, in subsequent refinements, by the unit cell dimensions, five background parameters, and the halfwidth of the Gaussian part of the peak shape. The titanium and oxygen positions were then refined along with their anisotropic thermal parameters.

Grins and West (*10*) identified all the possible interstitial sites in an idealized ramsdellite structure. These include two regular tetrahedral sites B1 and B2 located in the framework as well as two octahedral and five tetrahedral sites located in the channels (see Table I). Lithium ions were placed in each of these sites as well as the framework site shared with Ti and their occupancies were refined. Finite lithium occupancy was found only on sites C4, C1, and the framework site; these sites were labeled Li(1), Li(2), and Ti/Li(3), respectively. Isotropic thermal parameters were refined independently for Li(1) and Li(2) which were initially located in two fourfold sites; however, the isotropic parameter of Li(1) refined to a rather high value of approximately 4 Å^2 which suggested possible positional disorder. The fourfold site is associated with a fixed y parameter of 0.25; Li(1) was therefore placed on a general eightfold position and the y parameter refined, resulting in a reduction of the isotropic B-factor to 1.7 Å^2.

At this stage R-factors of $R_{wp} = 8.06\%$ and $R_{ex} = 6.40\%$ were obtained (for explanation of R-factors see Ref. (*11*)). Refinement of the structure without subtraction of the second phase gave an R_{wp} of 9.85%. However, there appeared to be no significant difference in the structural parameters between the corrected and uncorrected fits; all equivalent parameters were generally found to be within one e.s.d. of each other. The final refined parameters based on the subtracted profile are given in Table II and bond lengths and angles in Table III. The final fitted profile is given in Fig. 2.

Discussion

The refined cell dimensions in the present study are in close agreement with those reported earlier (*8*). The framework Ti/Li(3) atoms are in distorted octahedral environments with three long bonds of about 2.0 Å and three shorter bonds of between 1.95 and 1.96 Å, with O–Ti–O angles ranging from approximately 80 to 98°. In the previously reported structure, the coordination around Ti has four bonds of approximately 1.98 Å and one long and one short bond, but the mean bond length of 1.98 Å is very close to that observed in the present study. Titanium only partially occupies this site, the remaining sites being filled by Li(3).

Both sets of lithium ions in the channels are in distorted tetrahedral coordination, with one short bond of approximately 1.8 Å and three longer bonds to O ranging from approximately 1.9 to 2.2 Å. The distortion is such that Li is located close to the center of the channel. Li(1) and Li(2) sites individ-

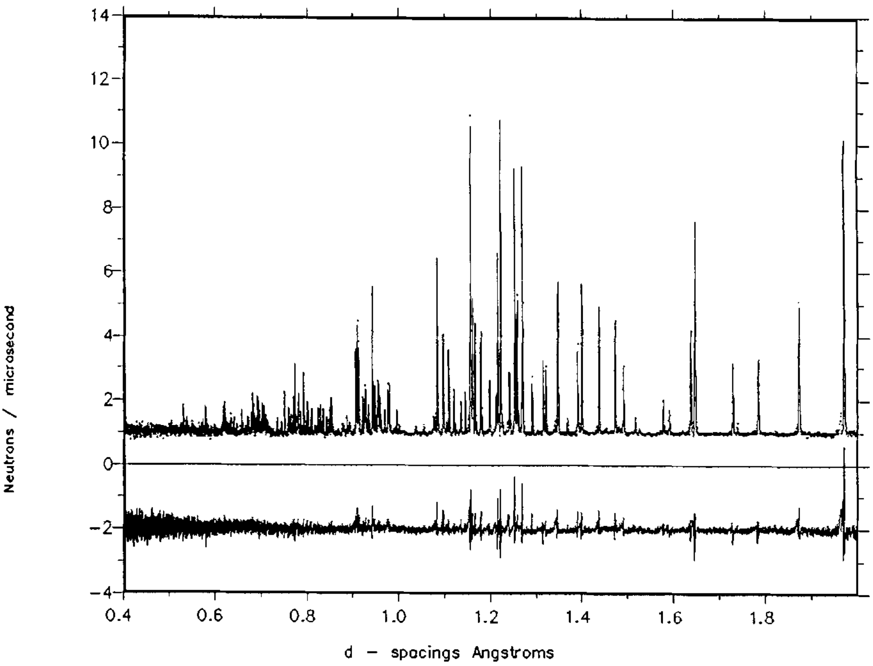

FIG. 2. Fitted time-of-flight neutron diffraction profile for $Li_2Ti_3O_7$ with difference (obs − calc) shown below.

ually form zigzag chains parallel to the *b*-axis by sharing common edges (Fig. 1). The chains of Li(1) and Li(2) sites are linked together by sharing common faces at approximately the same height in the unit cell (Fig. 1). Table IV shows the Li–Li and Li–Ti sites contact distances. Li(1) is the most energetically favorable site with no face-

TABLE II

REFINED ATOMIC PARAMETERS FOR $Li_2Ti_3O_7$

		a = 9.5423(1), b = 2.9438(1), c = 5.0136(1) Å				
Atom	Pos.	x/a	y/b	z/c	occ.	B-fac/Å^2
Li(1)	8d	0.445(1)	0.181(6)	−0.058(2)	0.124(9)	1.7(5)
Li(2)	4c	0.047(2)	0.25	0.540(3)	0.14(1)	1.3(5)
Li(3)	4c	0.1422(2)	0.25	−0.0316(3)	0.12(1)	—
Ti	4c	0.1422(2)	0.25	−0.0316(3)	0.86	—
O(1)	4c	0.27298(9)	0.25	0.6701(2)	1.0	—
O(2)	4c	−0.03206(8)	0.25	0.2045(1)	1.0	—

Anisotropic thermal parameters

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
O(1)	1.07(3)	0.65(3)	1.32(4)	0	0.53(3)	0
O(2)	0.85(3)	0.73(3)	0.62(3)	0	0.07(2)	0
Ti/Li(3)	0.88(7)	0.92(6)	1.33(7)	0	−0.11(4)	0

TABLE III

BOND LENGTHS (Å) AND ANGLES (°) FOR $Li_2Ti_3O_7$

Li(1)–O(1)	2.14(1)	
Li(1)–O(2)	1.80(1)	
Li(1)–O(2′)	1.93(1)	
Li(1)–O(2″)	2.22(2)	
Mean	2.02	
Li(2)–O(1)	2.25(2)	
Li(2)–O(2)	1.84(1)	
Li(2)–O(2′)	1.96(1)	×2
Mean	2.00	
Ti/Li(3)–O(1)	1.948(2)	
Ti/Li(3)–O(1′)	1.961(1)	×2
Ti/Li(3)–O(2)	2.041(2)	
Ti/Li(3)–O(2′)	2.006(1)	×2
Mean	1.99	
O(1)–Li(1)–O(2)	135.4(6)	
O(1)–Li(1)–O(2′)	90.0(5)	
O(1)–Li(1)–O(2″)	82.8(5)	
O(2)–Li(1)–O(2′)	129.0(8)	
O(2)–Li(1)–O(2″)	113.5(8)	
O(2′)–Li(1)–O(2″)	90.2(4)	
O(1)–Li(2)–O(2)	131.1(8)	
O(1)–Li(2)–O(2′)	83.2(5)	×2
O(2)–Li(2)–O(2′)	124.5(5)	×2
O(2′)–Li(2)–O(2″)	97.5(6)	
O(1)–Ti/Li(3)–O(1′)	97.56(5)	×2
O(1)–Ti/Li(3)–O(2′)	90.23(6)	×2
O(1′)–Ti/Li(3)–O(1″)	97.31(7)	
O(1′)–Ti/Li(3)–O(2)	92.13(6)	×2
O(1′)–Ti/Li(3)–O(2′)	83.58(2)	×2
O(2)–Ti/Li(3)–O(2′)	79.84(5)	×2
O(2′)–Ti/Li(3)–O(2″)	94.43(7)	

sharing contacts to the framework octahedra, the closest Li–(Ti/Li(3)) contact being 2.82(1) Å. The Li(2) tetrahedral site shares a face with the (Ti/Li(3)) octahedral site with a cation–cation distance of 2.33(1) Å. The site occupancies reflect the relative stabilities of the channel sites with over 60% of the channel lithium located in the Li(1) site. The negligible Li scattering in the C2 and C3 sites, which are the other tetrahedral sites considered by Morosin and Mikkelsen, relate to their energetically unfavorable location with close face-sharing contacts to Ti/Li(3) of approximately 1.8 and 2.0 Å, respectively. The total lithium occupancy of 2.0(2) Li per cell is within 2 e.s.d.'s of the calculated figure of 2.29 per cell.

Confining our attention to the four Li(1) and four Li(2) sites per cell, then by fully occupying these sites, up to eight lithium ions could hypothetically be accommodated in the channels; however, the tetrahedrally coordinated Li(1) and Li(2) sites share a common face with their centers being approximately 1 Å apart and these sites could not be simultaneously occupied. This reduces the theoretical maximum number of Li(1) and Li(2) ions per unit cell to four. Furthermore, it is unlikely that four lithiums could be accommodated in the Li(2) sites alone since their centers are separated by only 1.77 Å. In the present determination the Li(1) sites are no longer on the fourfold special position x, $\frac{1}{4}$, z but are located at eightfold general positions. The sites are arranged in four pairs such that both sites in a pair cannot be occupied simultaneously; however, if a Li(1)–Li(1) distance of 1.90 Å is regarded as tolerable

TABLE IV

LI-SITE CONTACT DISTANCES (Å) IN $Li_2Ti_3O_7$

		Distance
Li(1) 0.44, 0.18, −0.06		
	. . .Li(1) 0.44, 0.32, −0.06	0.40(4)
	. . .Li(1) 0.55, −0.18, 0.06	1.61(3)
	. . .Li(1) 0.55, −0.32, 0.06	1.90(1)
	. . .Li(1) 0.55, 0.82, 0.06	2.23(3)
Li(2) 0.05, 0.25, 0.54		
	. . .Li(1) −0.06, 0.32, 0.56	1.00(2)
	. . .Li(1) 0.06, 0.68, 0.44	1.36(2)
	. . .Li(1) 0.06, −0.32, 0.44	1.75(2)
	. . .Li(2) −0.05, 0.75, 0.46	1.77(2)
Shortest	Li(1). . .Ti/Li(3)	2.82(1)
Shortest	Li(2). . .Ti/Li(3)	2.33(1)
Shortest	[a]C2. . .Ti/Li(3)	ca. 2.0
Shortest	[a]C3. . .Ti/Li(3)	ca. 1.8

[a] Distances are calculated from the centers of the C2 and C3 sites.

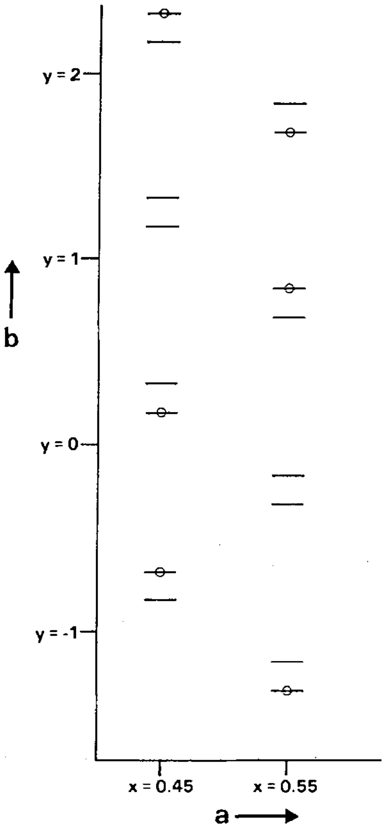

FIG. 3. Schematic projection onto *a*/*b* plane of the Li(1) sites in a single channel of the structure. An ordered lithium arrangement is represented which avoids contact distances of less than 2.23 Å while permitting an occupancy of 2.67 lithium ions per Li(1) site. — = Li(1) site; ○ = Li atom.

then four lithium ions could be accommodated in these eight sites. If, however, only the longer distance of 2.23 Å is energetically acceptable, then a maximum of 2.67 Li in these sites per unit cell is possible since a lithium–lithium distance of 2.23 Å could be attained by leaving every third Li(2) in the *b*-axis vacant (see Fig. 3). Based on the refinement, the total amount of Li contained in the channel sites per unit cell of $Li_2Ti_3O_7$ is 1.55; this is significantly less than the maximum value of 2.67 associated with contact distances of 2.23 Å. Therefore, lithium could be distributed over sites Li(1) and Li(2) with no close Li–Li interactions. This is reflected in the fact that, as stated above, the lithium distribution is controlled by Li–Ti repulsions and not by those between lithium ions.

Lithium insertion studies on $Li_2Ti_3O_7$ (*12*) have shown that at room temperature a material approximating to $Li_{2.5}Ti_3O_7$ is formed, while at 50 to 60°C more lithium is taken up to form $Li_3Ti_3O_7$. Assuming full occupation of the framework Li(3) site and that the channel lithiums are located at similar positions and have similar coordination to the present structure, there are 2.29 and 2.87 channel lithiums per cell in the room temperature and high-temperature materials, respectively. All the channel Li in the room-temperature material could be accommodated with no Li–Li distance less than 2.23 Å. The increase in Li uptake at higher temperatures may indicate that the energy barriers associated with shorter site contacts are overcome.

Finally the appearance of a second ramsdellite phase in the powder neutron data which was absent from powder X-ray data, even when collected using a Guinier focusing geometry, is a testimony to the high resolution of the HRPD diffractometer at ISIS.

Acknowledgments

We thank W. A. T. Harrison and R. M. Ibberson at the Neutron Division, Rutherford-Appleton Laboratory, UK, for their help in this work; the computer center at Heriot-Watt University for the provision of computing facilities for profile refinement, and the SERC for financial support.

References

1. H. Y.-P. HONG, *Mater. Res. Bull.* **13,** 117 (1978).
2. I. ABRAHAMS, P. G. BRUCE, A. R. WEST, AND W. I. F. DAVID, *J. Solid State Chem.* **75,** 390 (1988).
3. B. L. DUBEY AND A. R. WEST, *Nature Phys. Sci.* **235,** 155 (1972).
4. M. CASTELLANOS AND A. R. WEST, *J. Mater. Sci.* **14,** 450 (1979).

5. G. H. Jonker, *Trab. Reun. Int. React. Solidos, 3rd* **1,** 413 (1956).
6. G. Izquierdo and A. R. West, *Mater. Res. Bull.* **15,** 1655 (1980).
7. B. Morosin and J. C. Mikkelsen, Jr., *Acta Crystallogr. Sect. B* **35,** 798 (1979).
8. L. Koester and H. Rauch, IAEA Report 2517/RB (1981).
9. "International Tables for Crystallography" (T. Hahn, Ed.), Vol. A, Reidel, Dordecht/Boston (1983).
10. J. Grins and A. R. West, *J. Solid State Chem.* **65,** 265 (1986).
11. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
12. C. J. Chen and M. Greenblatt, *Mater. Res. Bull.* **20,** 1347 (1985).