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Structure Determination of Substituted Rutiles by Time-of-Flight Neutron Diffraction

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High-resolution time-of-flight neutron diffraction has been used to determine the structures of three cation-substituted rutile materials, viz., $Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$, $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$, and $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$. The three materials maintain the basic rutile framework with cations located in the titanium site of space group $P4_2/mnm$. Only $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$ showed any occupation of the channels that exist in these structures, with Li at $^1/_2,0,0$ and $^1/_2,0,^1/_4$ as well as in the framework site.

Introduction

Rutile, TiO_2, is an important material with applications ranging from use in the electronics industry to ceramic tile glazes. Recent studies have shown[1,2] that Ti^{4+} can be substituted by pentavalent Nb or Ta and a monovalent, divalent, or trivalent cation. A number of solid solutions have been examined including $Li_xM_{3x}Ti_{1-4x}O_2$, $Al_xM_xTi_{1-2x}O_2$, and $A_xM_{2x}Ti_{1-3x}O_2$, where M = Nb, Ta, or Sb, and A = Mg or Zn. The X-ray powder patterns for these materials indicate that the rutile structure (space group $P4_2/mnm$) is maintained but in most cases the cell dimensions increase to accommodate larger cations such as Nb, Ta, Zn, Mg, and Li. The exception is the Al-containing system, in which the combined substitution of the smaller Al and the larger pentavalent atoms in comparison to Ti causes little change in cell dimensions. While it seems likely that the large ions substitute directly onto the Ti site, lower valence cations could locate themselves in several possible interstitial sites as indicated here:[3]

Wyckoff position	*x,y,z*
4g	0.35,−0.35,0
4c	0.5,0,0
4d	0.5,0,0.25
8i	0.60,0.07,0

In the present study, the structures of three cation-substituted materials have been determined by high-resolution powder neutron diffraction using the new diffractometer, HRPD, at the Rutherford-Appleton Laboratory. This instrument offers exceptional resolution ($\Delta d/d = 5 \times 10^{-4}$) which may, for instance, indicate peak splitting that would not be observed with laboratory X-ray instruments, provided that broadening due to particle size and strain is minimal.

Experimental Section

Preparation. $Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$, $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$, and $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$ were prepared by solid-state reaction between TiO_2, Nb_2O_5, and either Al_2O_3, ZnO, or $^7Li_2CO_3$. In all three cases the starting materials were ground up as a slurry in ethanol for 15 min. The dried mixtures were placed in platinum crucibles and reacted in a muffle furnace. The specific reaction temperatures and times for each material are as follows:

$Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$. The mixture was heated at 1100 °C for 12 h, quenched, and ground before reheating to 1200 °C for 72 h and final quenching or slow cooling to room temperature.

$Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$. The mixture was heated directly at 1300 °C for 12 h, quenched to room temperature, and reground before being heated at 1250 °C for 48 h and quenched again. Further grinding and heating to 1000 °C for 12 h was necessary before finally being quenched or slow cooled to room temperature.

$Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$. The mixture was heated for 4 h at 650 °C to drive off CO_2, the temperature then elevated to 950 °C for 10 h, and the sample subsequently quenched to room temperature. After regrinding, the material was heated at 1050 °C for 48 h before finally being quenched or slow cooled to room temperature.

Materials were characterized initially by X-ray powder diffraction. Preliminary cell dimensions were obtained by using a focusing Stöe–Guinier camera and refined by least-squares fitting to all observable reflections between 8.8 and 1.6 Å. Long exposure times were used to identify low levels of impurities.

Data Collection. High-resolution time-of-flight (tof) powder neutron diffraction profiles were collected on the HRPD diffractometer at ISIS. Rutherford-Appleton Laboratory. Data were collected in the range (20–120) × 10^3 ms (corresponding to a *d*-spacing range of ca. 0.4–2.5 Å) with samples located at 1 m in front of banks of back-scattering detectors for the Zn-substituted material and at 2 m in front of the detectors for the other two materials. The data were summed over 20 concentric detector rings, and the background was fitted and subtracted by using a polynomial function. The data were refined by using a modified Rietveld method with the peak shape modeled by a convolution of a Gaussian and two exponential functions. The scattering lengths used were Ti = −0.3438, Nb = 0.7054, O = 0.5805, Zn = 0.5680, Al = 0.3449, and Li = -0.220×10^{-12} cm.[4]

Structure Determination

In the initial stages of refinement a common approach was used for the structure determinations of $Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$, $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$, and $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$. The powder neutron diffraction profile for one of the compounds is shown in Figure 1. Profiles of the other com-

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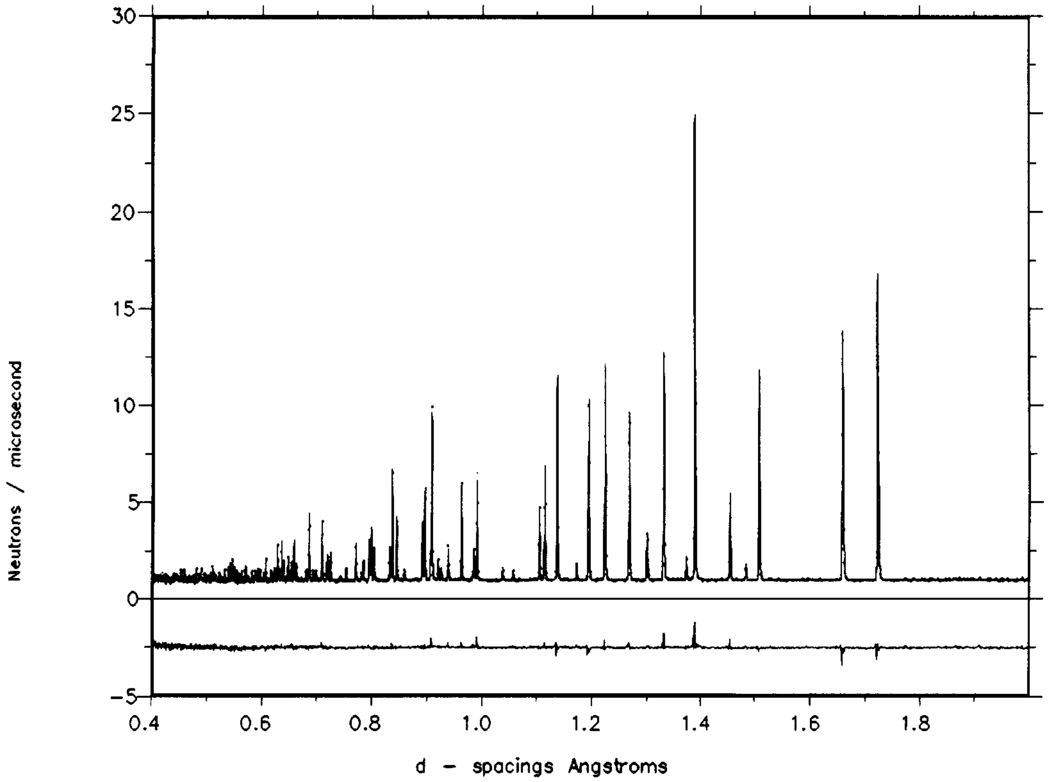

Figure 1. Fitted diffraction profile for $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$.

pounds are broadly similar. In each case the profile could be satisfactorily indexed on the rutile space group $P4_2/mnm$ (no. 136[5]). Detailed examination of both the neutron and X-ray patterns for each material revealed no evidence for additional reflections arising from a supercell due to cation ordering; such ordering was therefore ruled out. With rutile TiO_2[6] as a starting model, O was placed in the 4f position 0.3,0.3,0 and Ti/Nb in the 2a position 0,0,0 with their site occupancies fixed at the values determined by the composition. In each structure the scale factor was refined first followed by cell and zero-point correction parameters. During these initial refinements convergence could be obtained only if accurate lattice parameters extracted from Guinier photographs were used. Five background parameters were then refined followed by the Gaussian part of the peak shape. The oxygen x parameter was then varied, and difference Fourier maps were generated with O, Nb, and Ti atoms only. The specific details of the structure determinations for each material now follow:

$Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$. Close examination of the profile revealed a few very weak peaks that could not be satisfactorily assigned to the primary phase either by supercell formation or by symmetry lowering. It was therefore concluded that the extra peaks were from an unidentified secondary phase. The proportion of the secondary phase was very small on the basis of the relative intensities of the peaks of the primary and secondary phases, and its presence would have only a negligible influence on the composition of the primary phase; this was substantiated by the absence of the secondary phase peaks in the X-ray powder patterns even after long exposure. These small peaks were excluded from the profile. Difference Fourier maps based on O, Ti, and Nb indicated that Zn was located in the 0,0,0 position, and refinement of the Zn occupancy on this site confirmed this with a value of 0.13 (2) being obtained, which compares well with the calculated value of 0.15. Since the overall Zn occupancy was close to the calculated value, it was fixed at this value, and an isotropic temperature factor refined to give a value of 0.77 (4) Å^2. Anisotropic parameters were then successfully applied and refined for both cation and anion sites. Refinement terminated with R_{wp} = 6.14%, R_{ex} = 4.65% (for definition of R factors see ref 7). The refined atomic parameters are given in Table I, and bond lengths and angles are in Table II.

Table I. Final Refined Atomic Parameters for $Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$ with Estimated Standard Deviations in Parentheses

a = 4.6612 (1) Å c = 3.0106 (1) Å V = 65.41 Å^3

atom	Wyc.	x/a	y/b	z/c	occ
O	4f	0.30375 (4)	0.30375 (4)	0.0	1.00
Zn	2a	0.0	0.0	0.0	0.15
Nb	2a	0.0	0.0	0.0	0.30
Ti	2a	0.0	0.0	0.0	0.55

Anisotropic Thermal Parameters

	$B(11)$	$B(33)$	$B(23)$	$B(13)$	$B(12)$
O	0.676 (7)	0.76 (1)	0.0	0.0	−0.082 (9)
Zn/Nb/Ti	0.96 (5)	0.48 (8)	0.0	0.0	−0.40 (6)

Table II. Bond Lengths (angstroms) and Angles (degrees) for $Zn_{0.15}Nb_{0.30}Ti_{0.55}O_2$ with Estimated Standard Deviations in Parentheses

Nb/Ti/Zn–O	2.0023 (2) × 2
Nb/Ti/Zn–O′	1.9848 (1) × 4
mean	1.991
O–Nb/Ti/Zn–O′	90.00 (1)
O′–Nb/Ti/Zn–O′	98.65 (1)
O′–Nb/Ti/Zn–O′	81.35 (1)

$Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$. As in the Zn-substituted material,

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Table III. Final Refined Atomic Parameters for $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$ with Estimated Standard Deviations in Parentheses

a = 4.5849 (1) Å c = 2.9599 (1) Å V = 62.22 Å^3

atom	Wyc.	x/a	y/b	z/c	B, Å^2	occ
O	4f	0.304 70 (7)	0.304 70 (7)	0.0		1.00
Nb	2a	0.0	0.0	0.0	0.8	0.20
Ti	2a	0.0	0.0	0.0	0.8	0.60
Al	2a	0.0	0.0	0.0	0.8	0.20

Anisotropic Thermal Parameters

	$B(11)$	$B(33)$	$B(23)$	$B(13)$	$B(12)$
O	0.468 (9)	0.44 (1)	0.0	0.0	−0.09 (1)

Table IV. Bond Lengths (angstroms) and Angles (degrees) for $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$ with Estimated Standard Deviations in Parentheses

Nb/Ti/Al-O	1.9757 (3) × 2
Nb/Ti/Al-O′	1.9478 (2) × 4
mean	1.957
O-Nb/Ti/Al-O′	90.00 (2)
O-Nb/Ti/Al-O	98.90 (1)
O-Nb/Ti/Al-O	81.10 (1)

difference Fourier maps based on O, Nb, and Ti suggested that Al was mainly located in the framework octahedral site at 0,0,0. The combination of positive and negative scatterers at 0,0,0 was such that only a very small amount of scattering was detected from this site, leading to the domination of the profile by oxygen. The Al occupancy of the 0,0,0 site refined to a value of about 0.16, while in all other possible cation sites, Al occupancies yielded zero or negative values. The B factor on the 0,0,0 site proved to be unrefinable and was consequently fixed at the value of 0.8 Å^2, which was the value obtained in the Zn-substituted structure. Anisotropic thermal parameters were successfully refined for oxygen. In the final refinement the Al occupancy was held at the value determined by composition, refinement terminating with R_{wp} = 7.88%, R_{ex} = 6.89%. The atomic parameters are given in Table III, and bond lengths and angles are in Table IV.

$Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$. In the case of $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$ the difference Fourier indicated that some Li was probably located in the 0,0,0 position and also small amounts in the octahedral site at $^1/_2$,0,0 and the tetrahedral site at $^1/_2$,0,$^1/_4$ in the channels of the rutile structure. Refinement of the Li occupancy in the 0,0,0 position confirmed that not all the Li was located in this site. Refinement of Li in the $^1/_2$,0,0 and $^1/_2$,0,$^1/_4$ sites gave finite occupancies for these sites. It is possible to split each of the 4c octahedral channel sites into two tetrahedral sites located at the 8i position 0.60,0.07,0. Attempts to refine Li in these 8i sites did give a finite occupancy; however, this model was discarded as two of the Li-O bond lengths in the resulting distorted tetrahedral site were unrealistically short at 1.4 Å. In all the other possible cation sites, Li occupancies refined to zero or negative values. The three occupied sites 0,0,0, $^1/_2$,0,0, and $^1/_2$,0,$^1/_4$ are designated Li(1), Li(2), and Li(3) in Table V. Anisotropic thermal parameters were successfully refined for the O site. The small Li occupancies of the interstitial sites meant that only a single isotropic B factor could be refined for all three cation sites. In the final refinement the total Li occupancy over the three cation sites was fixed at the value calculated from the composition but allowed to refine between them. Refinement terminated with R_{wp} = 5.01%, R_{ex} = 4.98%. The refined atomic parameters are given in Table V, and significant bond lengths, contact distances, and angles are in Table VI; the fitted profile is shown in Figure 1.

Table V. Final Refined Atomic Parameters for $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$ with Estimated Standard Deviations in Parentheses

a = 4.6879 (1) Å c = 3.013 (1) Å V = 66.21Å^3

atom	Wyc.	x/a	y/b	z/c	B, Å^2	occ
O	4f	0.303 08 (5)	0.303 08 (5)	0.0		1.00
Nb	2a	0.0	0.0	0.0	1.12 (6)	0.45
Ti	2a	0.0	0.0	0.0	1.12 (6)	0.40
Li	2a	0.0	0.0	0.0	1.12 (6)	0.084 (4)
Li(2)	4c	0.5	0.0	0.0	1.12 (6)	0.023 (2)
Li(3)	4d	0.5	0.0	0.25	1.12 (6)	0.010 (2)

Anisotropic Thermal Parameters

	$B(11)$	$B(33)$	$B(23)$	$B(13)$	$B(12)$
O	0.802 (9)	0.88 (1)	0.0	0.0	−0.09 (1)

Table VI. Bond Length (angstroms) and Angles (degrees) for $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$ with Estimated Standard Deviations in Parentheses

Nb/Ti/Li(1)-O	2.0093 (2) × 2
Nb/Ti/Li(1)-O′	1.9935 (2) × 4
mean	1.999
Li(2)-O	1.6944 (2) × 2
Li(2)-O′	2.2673 (2) × 4
mean	2.076
Li(3)-O	1.8543 (2) × 4
Li(2)···Li(3)	0.753
Li(2)···Li(1)/Ti/Nb	2.340
Li(3)···Li(1)/Ti/Nb	2.462
Li(2)···Li(2)	1.507
Li(3)···Li(3)	1.507
O-Nb/Ti/Li(1)-O′	90.00 (1)
O′-Nb/Ti/Li(1)-O′	98.18 (1)
O′-Nb/Ti/Li(1)-O′	81.82 (1)
O-Li(2)-O′	90.00 (1)
O′-Li(2)-O′	83.28 (1)
O′-Li(2)-O′	96.72 (1)
O-Li(3)-O	99.50 (1)
O-Li(3)-O	132.06 (1)

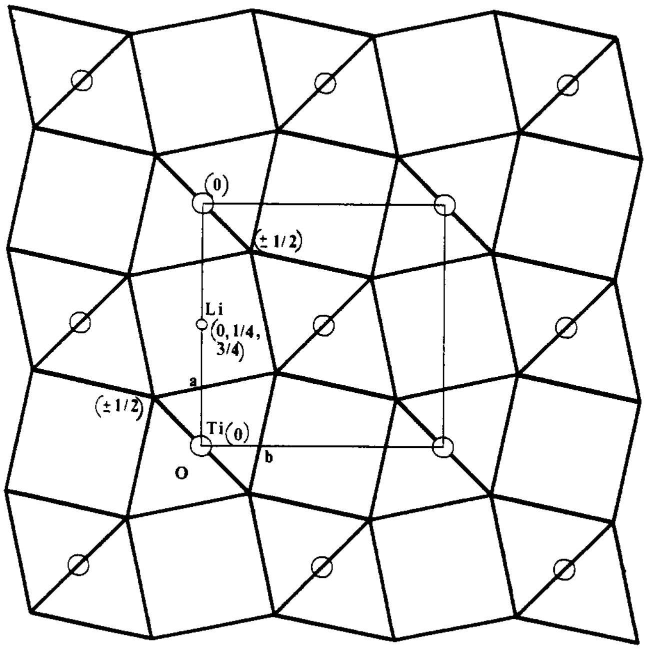

Figure 2. Projection of rutile structure, onto the a/b plane with heights along the c axis given in parentheses.

Discussion

The rutile structure[6] is well-known and consists of chains of edge-sharing TiO_6 octahedra parallel to the c axis, the chains being linked by corner sharing to form a three-dimensional network structure (Figure 2). Open channels parallel to the c axis are present with a distorted octahedral site at $^1/_2,0,0$ and a distorted tetrahedral site at $^1/_2,0,^1/_4$. In the three materials studied the Ti has been partially replaced by Nb and either Zn, Al, or Li. The cell volumes and Ti–O bond lengths observed in the three structures reflect the degree of Ti substitution in the particular material. In the Li- and Zn-substituted materials where much of the Ti has been replaced by the larger Nb, Zn, and Li atoms, the bond lengths and cell volumes are larger than those observed in rutile itself, for which $V = 62.45$ Å^3 and Ti–O = 1.945 × 4, 1.986 × 2 Å. In $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$ titanium is replaced by equal amounts of slightly larger Nb and considerably smaller Al cations, and consequently, the bond lengths and cell volume are somewhat smaller than in rutile.

The structure of $Zn_{0.15}Nb_{0.3}Ti_{0.55}O_2$ closely resembles that of rutile itself with occupation of the rutile octahedral cation site only. The Zn–O bond lengths of 1.9848 (1) and 2.0023 (2) Å are slightly shorter than the average bond lengths observed for octahedral Zn in $Zn_2Mo_3O_8$[8] of about 2.1 Å but reflect the average bond lengths for the Nb/Ti/Zn site.

Like the Zn-substituted material, $Al_{0.2}Nb_{0.2}Ti_{0.6}O_2$ differs little from the basic rutile framework. The bond lengths of 1.9757 (4) × 2 and 1.9478 (2) Å are within the range quoted for octahedral Al–O distances of 1.85–1.98 Å.[9]

The structure of $Li_{0.15}Nb_{0.45}Ti_{0.4}O_2$ shows finite occupation of both the channel and framework sites by Li ions, demonstrating once again that lithium ions are stable in both distorted and regular oxygen environments. The intercation distances suggest that Li(2) and Li(3) are unlikely to be simultaneously occupied. The distorted octahedral Li(2) site shares faces with two Li(1)/Ti/Nb octahedral sites, with Ti–Li(2) distances of 2.34 Å. The distorted tetrahedral Li(3) does not share a face with the Li(1)/Ti/Nb site, the closest Ti–Li(3) distance being 2.462 Å. The Li–Ti distances are similar to the shortest distance of Ti–Li = 2.33 Å seen in $Li_2Ti_3O_7$.[10] The site occupancy of Li(2) is apparently double that of Li(3), in which case it is not the Ti–Li contact distances that significantly affect the distribution, but the coordination, the octahedral coordination being preferred over that of tetrahedral coordination. The average Li–O values of 2.076 and 1.85 Å in Li(2) and Li(3) sites are typical for octahedrally and tetrahedrally coordinated Li, respectively.[9]

When powder refinement is carried out on a solid in which a given ion may be distributed over several sites and with a low occupancy of each site, it is generally necessary to tie the B factors of all the sites together in order to continue the refinement; this inevitably reduces the precision with which the highly correlated occupancies and B factors are determined.

Powder neutron diffraction at ISIS has proved a useful tool for determining the structure of materials; in particular the very high resolution of the data and the low d-spacing limit of 0.4 Å have permitted very accurate structure parameters to be obtained.

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Structural Investigation of the Hydrolysis–Condensation Process of Titanium Alkoxides $Ti(OR)_4$ (OR = OPr^i, OEt) Modified by Acetylacetone. 1. Study of the Alkoxide Modification

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Chemical modifications of alkoxides have been extensively used in sol–gel processing for a better control of the hydrolysis–condensation process. In this paper, the modification of titanium alkoxides ($Ti(OPr^i)_4$, $Ti(OEt)_4$) with acetylacetone is investigated by using infrared, ^1H and ^{13}C NMR, and X-ray absorption (XANES–EXAFS) spectroscopies. The reaction with titanium isopropoxide leads to a unique species, $Ti(OPr^i)_3acac$ (acac = acetylacetonate), whose structure is precisely described. It appears to be a monomer with titanium in 5-fold coordination. The reaction between acetylacetone and titanium ethoxide leads to the existence of several species in equilibrium, monomers in 5-fold coordination and oligomers in 6-fold coordination. These structural differences are related to the ability of the alkoxy groups to behave as bridging ligands. A study of the dilution of the modified precursor $Ti(OPr^i)_3acac$ in ethanol is also presented. Substitution of isopropoxy groups by ethoxy groups occurs and leads to the formation of new monomeric and oligomeric species. These products were characterized by ^1H NMR spectroscopy.

Introduction

Sol–gel processing has been widely investigated, especially for the manufacture of glasses and ceramics.[1,2] It requires the use of molecular precursors, mainly metal alkoxides from which a solid network is obtained through

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