

Powder Neutron Diffraction Study of $ZrTiO_4$, $Zr_5Ti_7O_{24}$, and $FeNb_2O_6$

P. BORDET

Laboratoire de Cristallographie, CNRS, 38042 Grenoble Cedex, France

AND A. McHALE,* A. SANTORO, AND R. S. ROTH

National Bureau of Standards, Gaithersburg, Maryland 20899

Received February 25, 1985; in revised form November 26, 1985

The zirconium titanates $ZrTiO_4$ and $Zr_5Ti_7O_{24}$ and the iron niobate $FeNb_2O_6$ have been investigated with the neutron diffraction powder technique and the Rietveld method. All three compounds crystallize with the symmetry of space group $Pbcn$ and have lattice parameters $a = 4.8042(2)$, $b = 5.4825(3)$, $c = 5.0313(2)$ Å for $ZrTiO_4$; $a = 14.3574(6)$, $b = 5.3247(3)$, $c = 5.0200(2)$ Å for $Zr_5Ti_7O_{24}$; and $a = 14.2661(2)$, $b = 5.7334(1)$, $c = 5.0495(1)$ Å for $FeNb_2O_6$. Pure zirconium titanate, $ZrTiO_4$, has the α - PbO_2 -type structure with a random distribution of the two cations. The compounds $Zr_5Ti_7O_{24}$ and $FeNb_2O_6$ are ordered superstructures of α - PbO_2 and in these two cases the observed distortions depend on the differences between ionic radii, leading to a fersmite-type structure in the case of $Zr_5Ti_7O_{24}$ and to a columbite-type structure in the case of $FeNb_2O_6$. © 1986 Academic Press, Inc.

Introduction

Zirconium titanate may exist in a number of modifications. Rapid quenching in water from temperatures above 1150°C of the compound obtained from ZrO_2 and TiO_2 gives the high-temperature phase of $ZrTiO_4$. This phase has been studied by X-ray diffraction techniques (1). The structure is derived from that of columbite (2) by assuming a random distribution of the zirconium and titanium ions in the sites $4c2$ and $8d1$ of space group $Pbcn$. It has been observed that the unit cell volume decreases continuously with decreasing quenching temperature in the range between 1450 and 1150°C (3). Such behavior of the cell pa-

rameters has been attributed to a continuous change of the order-disorder parameter of the Zr^{4+} and Ti^{4+} ions, but no experimental evidence of this hypothesis has been given so far.

A phase transition occurs within a temperature range of about 1100–1190°C (3). The transformation from the high- to the low-temperature form is sluggish. Slow cooling from temperatures below 1150°C yields a modulated structure, probably due to partial ordering of the cations.

The presence of small quantities of SnO_2 decreases the rate of ordering of the metal ions and, therefore, stabilizes the high-temperature form, while about 1% of Y_2O_3 enhances the ordering rate and results in the formation of a compound having a Zr/Ti ratio of about 5/7.

Since zirconium titanate ceramics are of

* Present address: Imperial College of Science and Technology, Department of Metallurgy, Prince Consort Road, London SW7 2BP, U.K.

technological interest as dielectric resonator materials in microwave devices, it is important to investigate the crystal structures and the ordering schemes in these compounds. In this paper we report the results of a neutron powder diffraction study of the high-temperature phase of $ZrTiO_4$ and of the compound with $Zr/Ti \approx 5/7$. We have also reanalyzed the structure of columbite, $FeNb_2O_6$, because of its close structural relationship with the latter compound.

Experimental

Specimens of $ZrTiO_4$ were prepared by conventional solid-state reactions (3). The raw materials were low Hf-grade ZrO_2 and high-purity TiO_2 (anatase). The oxides were mixed, ground under acetone, and then calcined at about $1000^\circ C$ for 24 hr. The resulting material was ground again and then heated at $1500^\circ C$ for 60 hr. This operation was repeated twice to ensure homogeneity in the final product compound. After the final heat treatment at $1500^\circ C$ the powder and the crucible were rapidly removed from the furnace and quenched in water. Other specimens of $ZrTiO_4$ were cooled slowly ($6^\circ/hr$ and $1^\circ/hr$) giving various phases with incommensurate X-ray diffraction patterns and variable cell dimensions (3).

The material with $Zr/Ti \approx 5/7$ was prepared by solid-state reaction of the appropriate amounts of high-purity Y_2O_3 , TiO_2 , and ZrO_2 .¹ The mixtures were heated with the same procedure described for $ZrTiO_4$. However, after the last heat treatment at $1500^\circ C$ the sample was cooled to about room temperature at the rate of $1^\circ/hr$. Assuming that the full amount of Y_2O_3 is incorporated in the structure, the composition of this material is $(1.00)Y_2O_3 \times (41.25)ZrO_2 \times (57.75)TiO_2$. If in first ap-

proximation we ignore the presence of yttrium, the formula of the compound can be written as $Zr_5Ti_7O_{24}$.

The sample of $FeNb_2O_6$ was prepared using the method described by Turnock (4). Stoichiometric mixtures of Fe_2O_3 and Nb_2O_5 were heated twice at 1130 – $1160^\circ C$ in a Pt boat presaturated with Fe by heating a previous batch of $FeNb_2O_6$ prepared under the same conditions. Both heat treatments were done in a controlled atmosphere of Ar and N_2 (containing about 5% H_2) with a partial pressure of oxygen less than 10^{-14} atm. This pressure was kept constant during the cooling of the sample. The final material contained a trace of NbO_2 .

It was not possible to grow single crystals of these compounds large enough for neutron single-crystal diffraction work. In most cases twinning was present even in the small crystals prepared for the X-ray measurements. For this reason it was decided to analyze these materials with powder diffraction data and the Rietveld method (5).

The neutron powder diffraction data were collected at room temperature with the high-resolution five-detector diffractometer at the NBS reactor (6) using the experimental conditions shown in Table I. Whenever possible peak shapes were checked by fitting the observed single reflections with Pearson type VII distributions (7) with the least-squares method.

TABLE I
EXPERIMENTAL CONDITIONS USED TO COLLECT THE
NEUTRON POWDER INTENSITY DATA

Monochromatic beam	Reflection 220 of a Cu monochromator
Wavelength	1.542(1) Å
Horizontal divergences	10, 20, and 10' arc for the in-pile, monochromatic beam, and diffracted beam collimators, respectively
Sample container	Vanadium can of ~10 mm diameter

¹ The role of Yttrium in forming $Zr_5Ti_7O_{24}$ is discussed by McHale and Roth in a paper submitted for publication to *J. Am. Ceramic Soc.*

The neutron data were analyzed using the program written by Prince (8) which allows processing the intensities from the five counters of the diffractometer simultaneously. The background was assumed to be a straight line with finite slope and was refined for each channel together with the profile and structural parameters. Initial values of the profile parameters U , V , and W were calculated with the formulas derived by Caglioti *et al.* (9). The scattering lengths used in the refinements are $b(O) = 0.58$, $b(Ti) = -0.34$, $b(Zr) = 0.71$, $b(Fe) = 0.95$, and $b(Nb) = 0.71 \times 10^{-12}$ cm (10).

Refinement of the Structures

Preliminary single-crystal and powder X-ray analysis showed that both $ZrTiO_4$ and $Zr_5Ti_7O_{24}$ crystallize with the symmetry of space group $Pbcn$ and that the a parameter of $Zr_5Ti_7O_{24}$ is approximately three times that of $ZrTiO_4$. Lattice parameter measurements suggest that $Zr_5Ti_7O_{24}$ and $FeNb_2O_6$ (columbite) may be isomorphous.

The initial positional parameters used to refine the structure of $ZrTiO_4$ were those given by Newnham (1). The results obtained after the final refinement are given in Table II, and the agreement between observed and calculated intensities is shown in Fig. 1. Although the R factors calculated in the refinement indicate that the structure is essentially disordered, the relatively high value of R_N (14.28%) may reflect a slight ordering of the metal ions in agreement with a hypothesis made by McHale and Roth (3) to explain the continuous contraction of the unit cell with decreasing temperature. Refinements were therefore attempted using structural models in which partial or total ordering of the titanium and zirconium ions is possible.

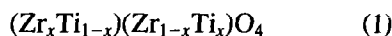
One possible ordering scheme for $ZrTiO_4$, suggested by Newnham (1), is based on the structure of wolframite, $NiWO_4$ (11). This structural type has the general formula

TABLE II
RESULTS OF THE REFINEMENT OF THE
HIGH-TEMPERATURE PHASE OF $ZrTiO_4$

Atom	Pos.	x	y	z	$B(\text{\AA}^2)$	n
Zr	4c2	0	0.265(1)	$\frac{1}{4}$	0.3	0.25
Ti	4c2	0	0.265	$\frac{1}{4}$	0.3	0.25
O	8d1	0.2704(4)	0.1004(3)	0.0700(3)	0.5	1.00

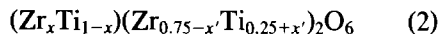
Notes. Space group $Pbcn$, general formula MO_2 ($M = \frac{1}{2} Zr + \frac{1}{2} Ti$), $Z = 4$, $a = 4.8042(2)$, $b = 5.4825(3)$, $c = 5.0313(2)$ \AA. Figures in parentheses are standard deviations in the last decimal figure. $R_N = 14.28$, $R_P = 7.79$, $R_W = 9.86$, $R_E = 5.01$. The R factors are defined in a number of publications (e.g., A. Santoro, R. S. Roth, and D. Minor, *Acta Crystallogr. Sect. B* 33, 3945 (1977)). Peak shape: Gaussian. Number of Bragg reflections: 99.

ABO_4 , with A and B located in special positions $2e2$ of space group $P2/c$. In this scheme the formula of $ZrTiO_4$ should be written



thus allowing partial ($x \neq 1$) or complete ($x = 1$) ordering of the metal ions. Refinements of this model showed that there is no evidence of monoclinic distortions and the best values for the R factors were obtained for $x = 0.5$, i.e., for the disordered structure. We may conclude, then, that there is no indication of ordering of the wolframite type.

Refinements were also carried out using a model isomorphous with columbite (2). The general formula for this type of structure is AB_2O_6 with A in positions $4c2$ and B in positions $8d1$ of space group $Pbcn$. In this scheme the formula of $ZrTiO_4$ should be written



where $x = 2x'$. Here again, the best agreement between observed and calculated intensities was obtained for $x' = 0.25$, corresponding to the completely disordered structure.

The last model taken into consideration is the one isostructural with wadginitite (12).

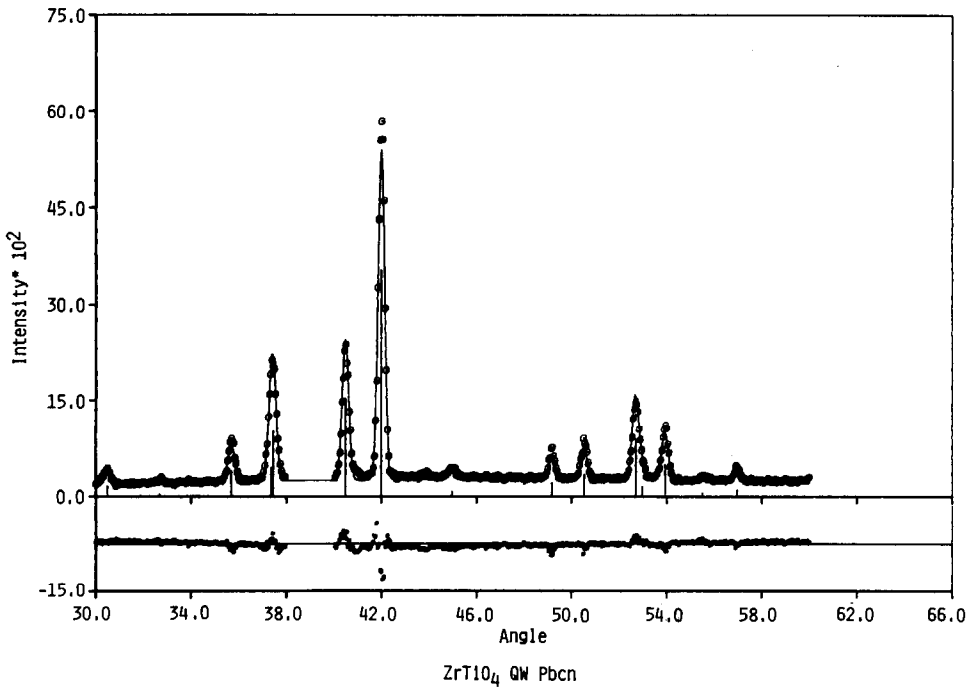
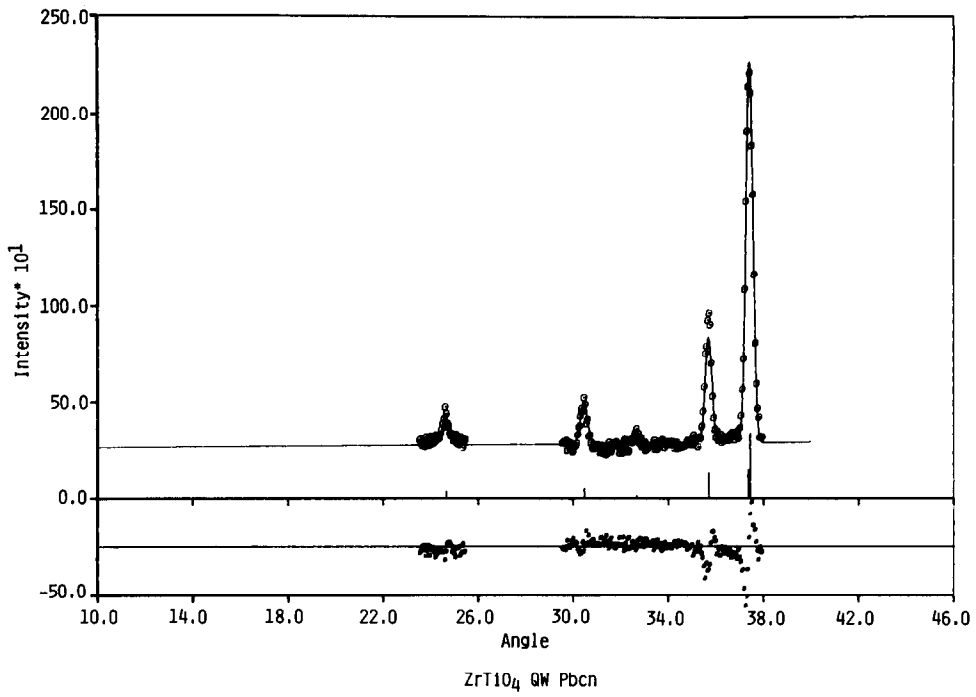


FIG. 1. Observed and calculated profile intensities for the structure of $ZrTiO_4$. The first two excluded regions correspond to background, and the third, between 38 and 40° to a very weak unidentified peak probably due to small amounts of impurities.

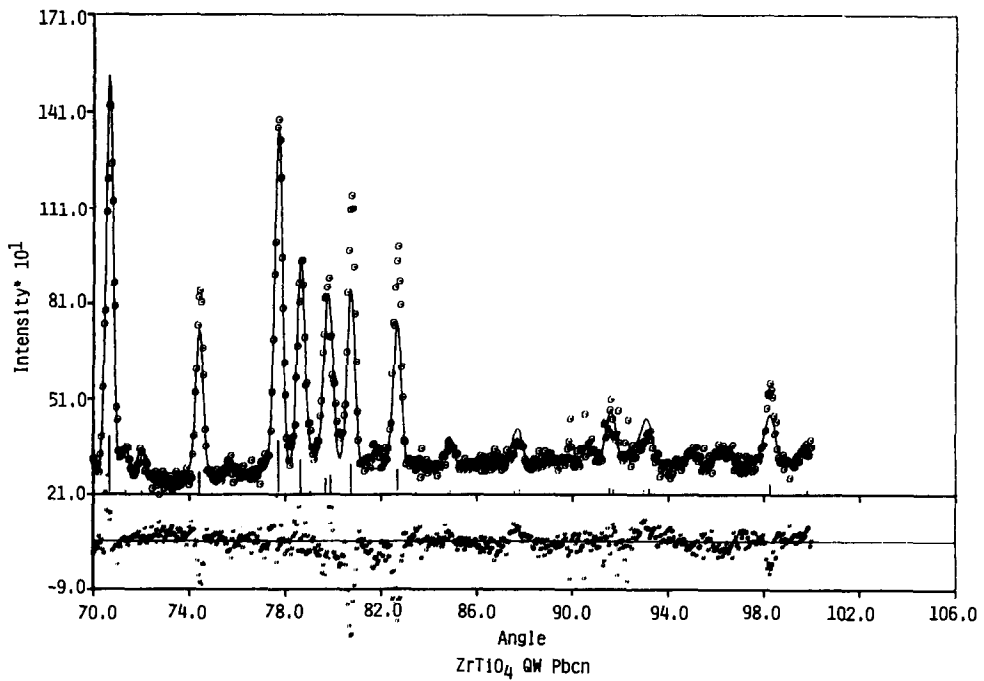
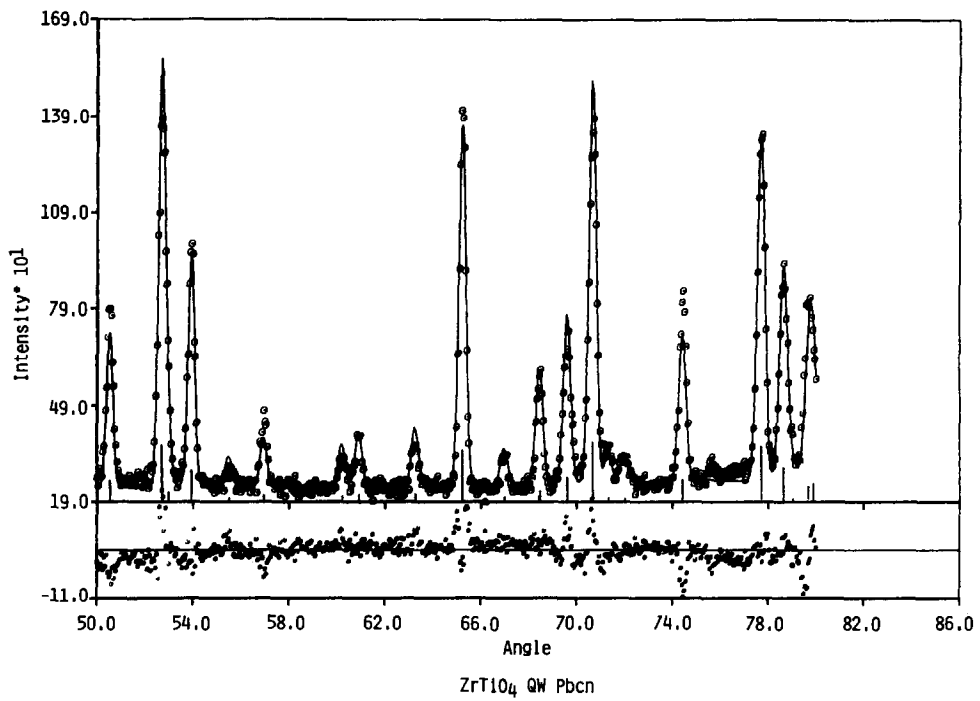


FIG. 1—Continued.

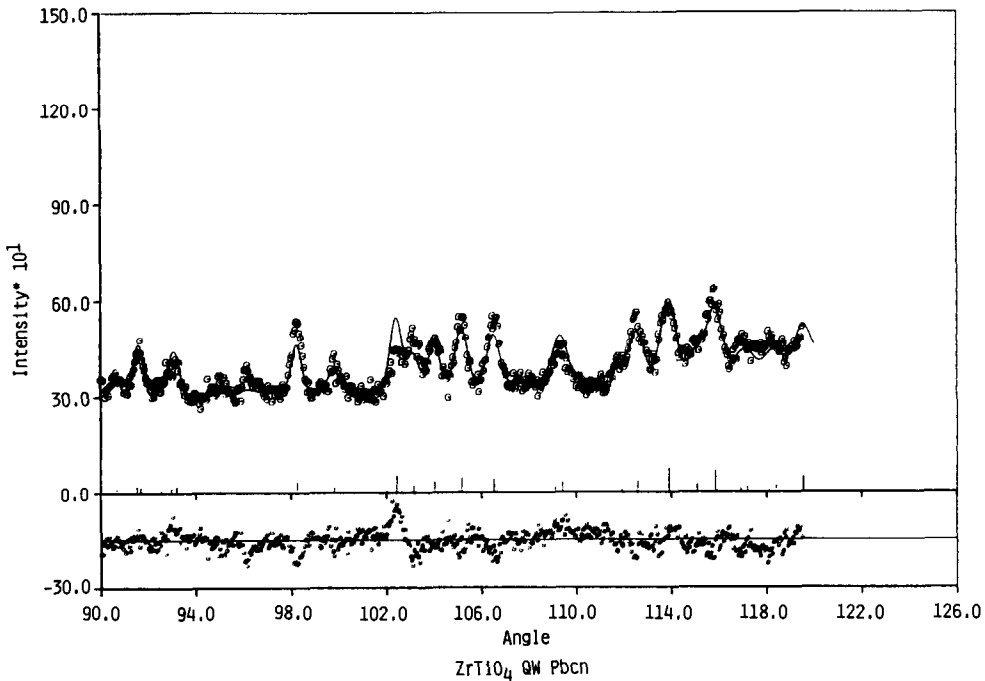
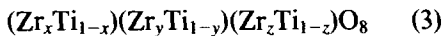


FIG. 1—Continued.

This material has general formula ACB_2O_8 with A and C in positions $4e_2$ and B in positions $8f_1$ of space group $C2/c$. In this scheme the formula of $ZrTiO_4$ becomes



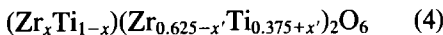
where $2z = 2 - (x + y)$ and $0 \leq x + y \leq 2$, of course. Refinements of the occupancy factors x and y gave also in this case a value not significantly different from $x = y = 0.5$, corresponding to a completely disordered structure.

The previous analysis shows that the high-temperature phase of $ZrTiO_4$ is either partially ordered according to a scheme other than any of those represented by formulas (1)–(3), or completely disordered. A possible explanation is that the disorder is near-random, i.e., not equally distributed in all directions. However, no diffuse streaks were observed in the single-crystal preliminary studies. If, on the other hand, the structure is completely disordered, then the

relatively high value of R_N is not due to the arrangement of the cations in the structure and could be caused instead by factors such as imprecise description of peak shapes, presence of impurities in the sample, anisotropic temperature factors etc.

As we have mentioned previously, the lattice parameters b and c of $Zr_5Ti_7O_{24}$ are close to the corresponding ones found for the high-temperature phase of $ZrTiO_4$, while the a parameter is approximately tripled. It is therefore reasonable to think that $Zr_5Ti_7O_{24}$ is a superstructure of $ZrTiO_4$ and that the tripling of the a axis is due to ordering of the zirconium and titanium ions. As the space group ($P2_1/b 2/c 2_1/n$, No. 60) is the same for the two compounds, the tripling of the a axis causes the elimination of two out of three b glides, two out of three twofold axes along b , and two out of three twofold screw axes along c . As a consequence of this rearrangement of the symmetry elements in the unit cell, the three

cationic positions, which are $4c2$ in the disordered structure of $ZrTiO_4$, become a position $4c2$ and a position $8d1$ in the structure of $Zr_5Ti_7O_{24}$. The positions $8d1$ of the oxygen atoms in $ZrTiO_4$ generate, of course, three sets of positions $8d1$ in the tripled cell. The general formula of the compound is, therefore AB_2O_6 and ordering of the cations is clearly possible. In the refinements we may ignore the presence of the small amount of yttrium as this element has a scattering length (0.775×10^{-12} cm) very close to that of Zr (0.716×10^{-12} cm). If we assume that the stoichiometry corresponds exactly to the formula $Zr_5Ti_7O_{24}$ we may express the type of ordering of the Ti^{4+} and Zr^{4+} by means of a parameter x according to the formula



with $x = 2x'$ (for $x = 0.417$ we would have $A = B = (0.417)Zr + (0.583)Ti$, i.e., a structure completely disordered). On the other hand if x and x' are not related to one another, i.e., if $x \neq 2x'$, the stoichiometry may change. Two sets of refinements were therefore carried out, one using a model in which the stoichiometry was constrained so that $Zr/Ti = 5/7$, and one using a model without stoichiometric constraints. The two calculations gave identical values of the atomic positional parameters. The unconstrained refinement, however, resulted in slightly lower R factors and in somewhat more reasonable thermal parameters for the zirconium and titanium ions. The results of this refinement are shown in Table III and the agreement between observed and calculated intensities is shown in Fig. 2.

As we have mentioned before, the structure of columbite, $FeNb_2O_6$, has been refined in order to compare it with that of $Zr_5Ti_7O_{24}$. Columbite has been studied previously (2). The compound crystallizes with a superstructure of α - PbO_2 in which the parameter a is tripled as a result of ordering of the iron and niobium ions. The

TABLE III
RESULTS OF THE STRUCTURE REFINEMENT OF
 $Zr_5Ti_7O_{24}$

Atom	Pos.	x	y	z	B	n
Zr(1)	$4c2$	0	0.2629(8)	$\frac{1}{2}$	0.64(9)	0.484(3)
Ti(1)	$4c2$	0	0.2629	$\frac{1}{2}$	0.64	0.016
Zr(2)	$8d1$	0.3324(5)	0.3335(14)	0.1798(14)	1.2(2)	0.111(5)
Ti(2)	$8d1$	0.3324	0.3335	0.1798	1.2	0.889
O(1)	$8d1$	0.0873(2)	0.0668(7)	-0.0234(5)	1.19(8)	1
O(2)	$8d1$	0.4194(2)	0.0824(6)	0.0599(5)	0.76(8)	1
O(3)	$8d1$	0.7600(2)	0.1226(6)	0.1402(6)	1.61(7)	1

Notes. Space group: $Pbcn$. General formula AB_2O_6 , $Z = 4$. $a = 14.3574(6)$, $b = 5.3247(3)$, $c = 5.0200(2)$ Å. Peak shape: modified Lorentzian (Pearson VII function with $m = 2$). $R_N = 9.89$, $R_P = 7.34$, $R_W = 9.30$, $R_F = 4.49$. Refined formula: $(Zr_{3.87}Ti_{0.13})(Zr_{0.89}Ti_{7.11})O_{24}$. Number of Bragg reflections: 291.

initial parameters introduced in the refinement were those of Sturdivant (2) and the final results are shown in Table IV. The agreement between observed and calculated intensities is shown in Fig. 3.

Description of the Structures

$ZrTiO_4$

The high-temperature phase of $ZrTiO_4$ has a structure of type α - PbO_2 . A projection of the structure of the (010) plane is shown in Fig. 4 and selected interatomic distances are given in Table V. The cations M ($\frac{1}{2}Zr + \frac{1}{2}Ti$) occupy positions $4c2$ in a disordered fashion and the oxygen anions, located in positions $8d1$, form coordination octahedra which are considerably distorted. These octahedra share edges along the direction of the c axis and form chains having a typical zigzag configuration along this axis. The average distance cation-anion is 2.079 Å, i.e., it lies in between the distances calculated from the values of the ionic radii of Ti^{4+} , Zr^{4+} , and O^{2-} (13).

$Zr_5Ti_7O_{24}$

As we have mentioned previously, $Zr_5Ti_7O_{24}$ has a superstructure which can be easily described in terms of the α - PbO_2 type

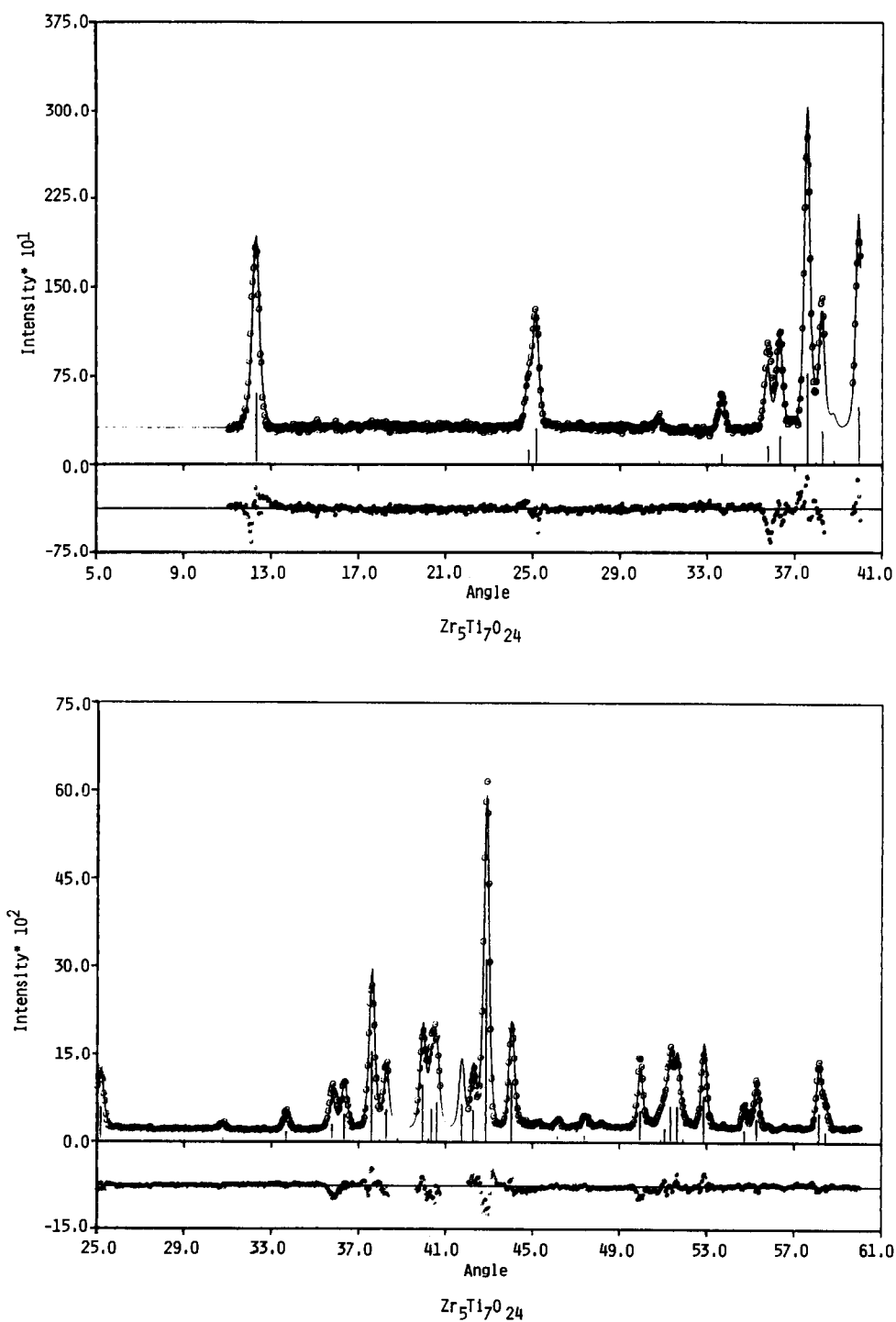


FIG. 2. Observed and calculated profile intensities for the structure of $Zr_5Ti_7O_{24}$. The few excluded regions correspond to background or very weak identified peaks probably due to impurities.

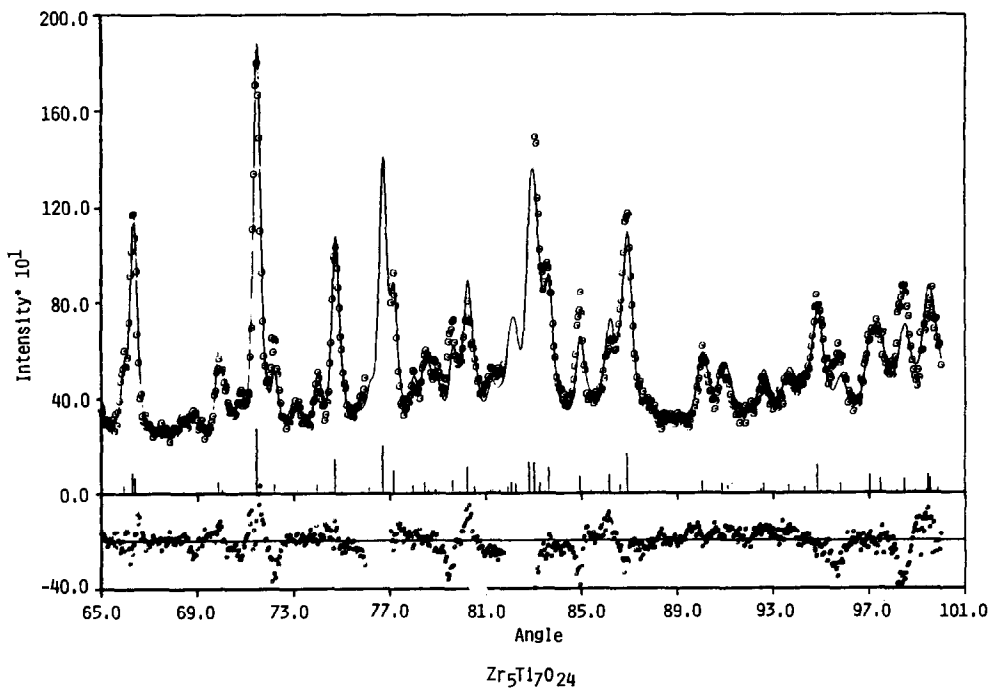
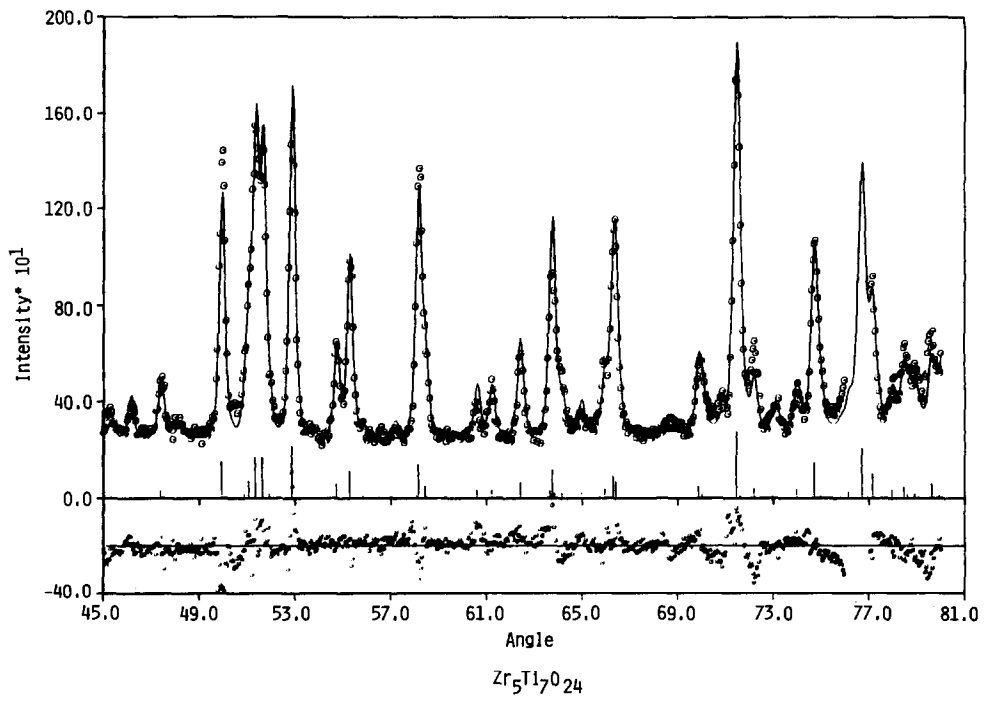


FIG. 2—Continued.

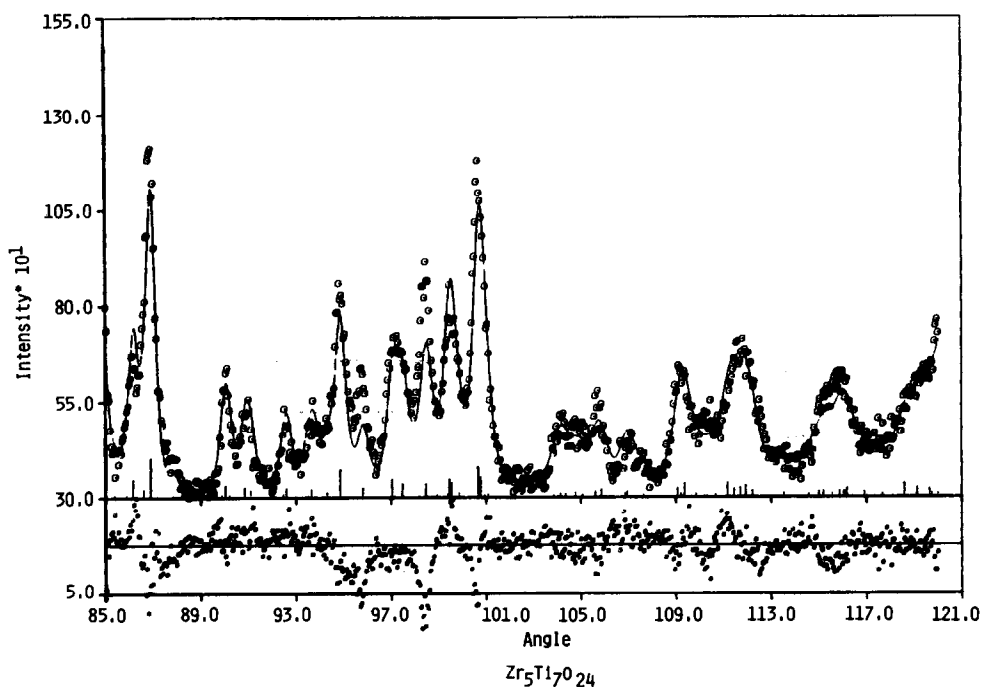


FIG. 2—Continued.

structure of $ZrTiO_4$. In α - PbO_2 , in addition to this six oxygen ions which are the nearest neighbors, each cation has also two more oxygen ions as second nearest neighbors. If we deform this structure so that these eight anions occupy the corners of a cube with a cation at the center, we obtain the fluorite structure. It is then possible to describe the structure of α - PbO_2 as a very distorted fluorite. In CaF_2 each cation has a coordination eight and each anion is next to four cations located at the corners of a tetrahedron. In α - PbO_2 , on the other hand, each cation has six nearest neighbors and two second nearest neighbors, and each anion is bounded to three cationic nearest neighbors and one cationic second nearest neighbor. In $Zr_5Ti_7O_{24}$ the positions $4c2$ are occupied by cations $A = 0.968 \text{ Zr} + 0.032 \text{ Ti}$, i.e., almost exclusively by Zr ions, and the positions $8d1$ by cations $B = 0.111 \text{ Zr} + 0.889 \text{ Ti}$. A projection of the structure on

the plane (010) (Fig. 5) shows that along the direction of the a axis one polyhedron out of three is occupied by a cation of type A. As shown in Table VI, this cation has eight oxygen ions as first neighbors, with a distance $A-O$ varying between 2.107 and 2.440 Å. The coordination polyhedron, therefore, is a very distorted cube. The cations of type

TABLE IV
RESULTS OF THE STRUCTURAL REFINEMENT OF
COLUMBITE, $FeNb_2O_6$

Atom	Pos.	x	y	z	B	n
Fe	$4c2$	0	0.3311(5)	$\frac{1}{2}$	0.35(4)	0.5
Nb	$8d1$	0.3389(2)	0.3191(3)	0.2506(6)	0.48(4)	1
O(1)	$8d1$	0.0963(2)	0.1041(4)	0.0727(5)	0.51(6)	1
O(2)	$8d1$	0.4189(2)	0.1163(5)	0.0990(5)	0.65(6)	1
O(3)	$8d1$	0.7560(2)	0.1236(5)	0.0793(6)	0.43(5)	1

Notes. Space group: $Pbcn$. General formula AB_2O_6 , $Z = 4$. $a = 14.2661(2)$, $b = 5.7334(1)$, $c = 5.0495(1)$ Å. Peak shape: Gaussian. $R_N = 2.73$, $R_P = 4.85$, $R_W = 6.83$, $R_E = 4.62$. Number of Bragg reflections: 317.

TABLE V
INTERATOMIC DISTANCES IN $ZrTiO_4$

O-O ^a		M-O ^b	
1×	2.564(3)	2×	1.823(4)
2×	2.746(1)	2×	2.087(3)
2×	2.748(1)	2×	2.328(6)
1×	2.854(3)	Average 2.079	
1×	2.908(4)		
2×	2.993(2)		
2×	3.010(2)		
1×	3.167(4)		
Average 2.873			

^a Distances between the oxygen ions belonging to the octahedron of the metal ion *M*.

^b $M = \frac{1}{2} Zr + \frac{1}{2} Ti$.

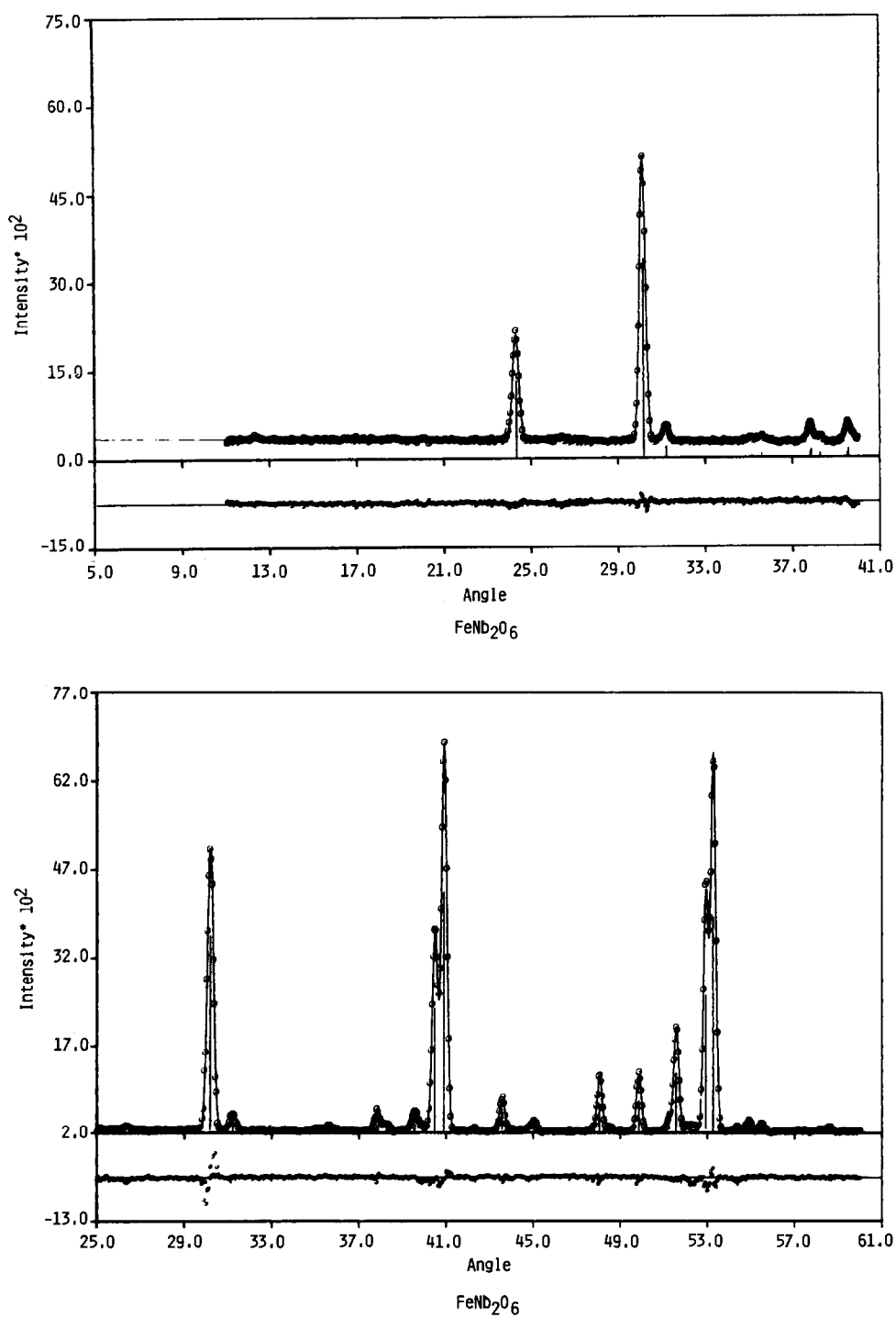
B, located in positions 8d1, are surrounded by six oxygen ions at distances between 1.929 and 2.061 Å, and by two oxygen ions at 3.18 and 3.21 Å. Their coordination polyhedron, therefore, is an octahedron slightly distorted. The average distance observed for the coordination polyhedra of cations *A* (2.237 Å) and *B* (1.968 Å) agree closely with the values of the ionic radii of O²⁻, Zr⁴⁺, and Ti⁴⁺ (1.40, 0.85, and 0.60 Å, respectively).

The Zr⁴⁺ cation has eight coordination similar to that present in ZrO₂, while Ti⁴⁺ has six coordination similar to that present in α-PbO₂. The difference of coordination numbers is due to the difference of the ionic radii of the two cations. The deformation of the 4c2 sites occupied by Zr⁴⁺ ions brings about a change in the oxygen coordination. O(2) and O(3) have three first-neighbor cations (at average distances of 2.101 and 1.984 Å) as in α-PbO₂. On the other hand, O(1) has four first-neighbor cations at distances of 2.133, 2.440, 1.953, and 1.974 Å. This configuration is similar to the coordination of the oxygen ions in tetragonal ZrO₂ where each ion is bonded to four Zr⁴⁺ ions at distances of 2.065 and 2.455 Å (14).

The structure of Zr₅Ti₇O₂₄ consists of chains of edge-sharing octahedra along the *c* axis. The octahedra are occupied by cations of type *B* and the chains have the zig-zag conformation typical of the α-PbO₂ structure. The chains are connected to one another by corner sharing along the direction of the *b* axis and by cations *A* along the *a* axis. As a consequence of this arrangement, each cation *A* is surrounded by a pseudo-cubic polyhedron of eight oxygen ions. These polyhedra form chains similar

TABLE VI
INTERATOMIC DISTANCES IN THE STRUCTURE OF
Zr₅Ti₇O₂₄

A-O		B-O	
2×	2.133(4)	1×	1.953(8)
2×	2.440(4)	1×	1.974(8)
2×	2.107(3)	1×	1.930(8)
2×	2.268(4)	1×	1.929(8)
Average 2.237(4)		1×	1.961(8)
		1×	2.061(8)
Average 1.968(8)			
A-A		B-B	
1×	3.560(4)	2×	3.56(1)
1×	3.760(4)	1×	3.07(1)
A-B			
1×	3.274(7)		
1×	3.774(7)		
1×	3.334(8)		
1×	3.895(8)		
O-O (pseudo-cube around cation A)		O-O (octahedron around cation B)	
2×	2.609(4)	1×	2.609(4)
2×	2.621(5)	1×	2.806(4)
2×	2.779(5)	1×	2.779(5)
2×	2.615(5)	1×	2.930(4)
2×	2.659(4)	1×	2.930(4)
2×	2.547(5)	1×	3.035(5)
Average 2.638(5)		1×	2.482(5)
		1×	2.991(4)
		1×	2.952(4)
		1×	2.678(4)
		1×	2.829(4)
		1×	2.867(4)
Average 2.824(5)			

FIG. 3. Observed and calculated profile intensities for the structure of FeNb_2O_6 .

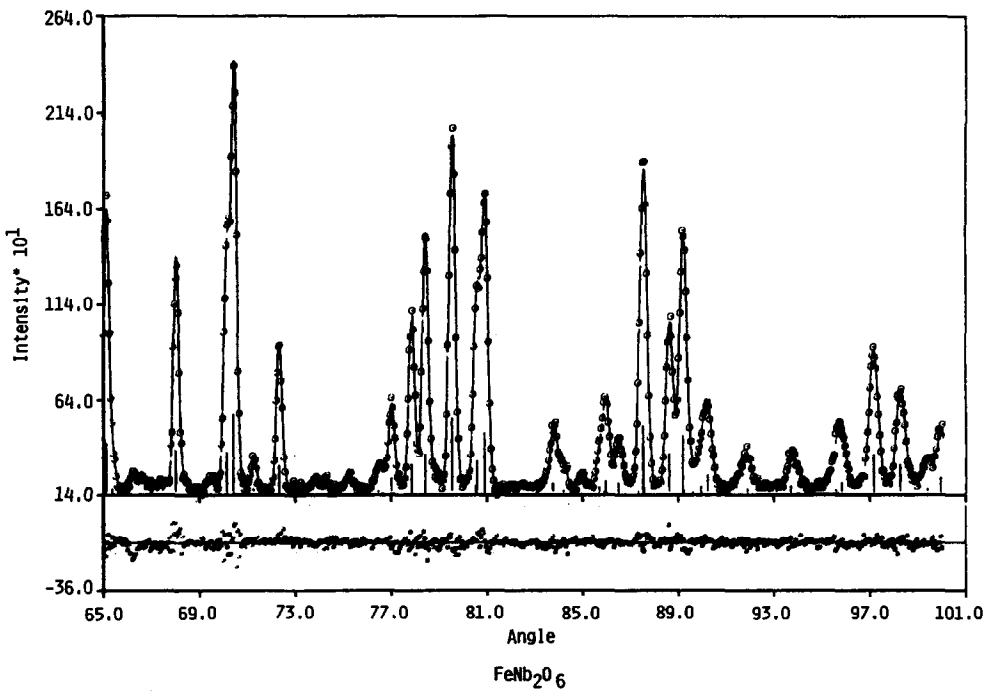
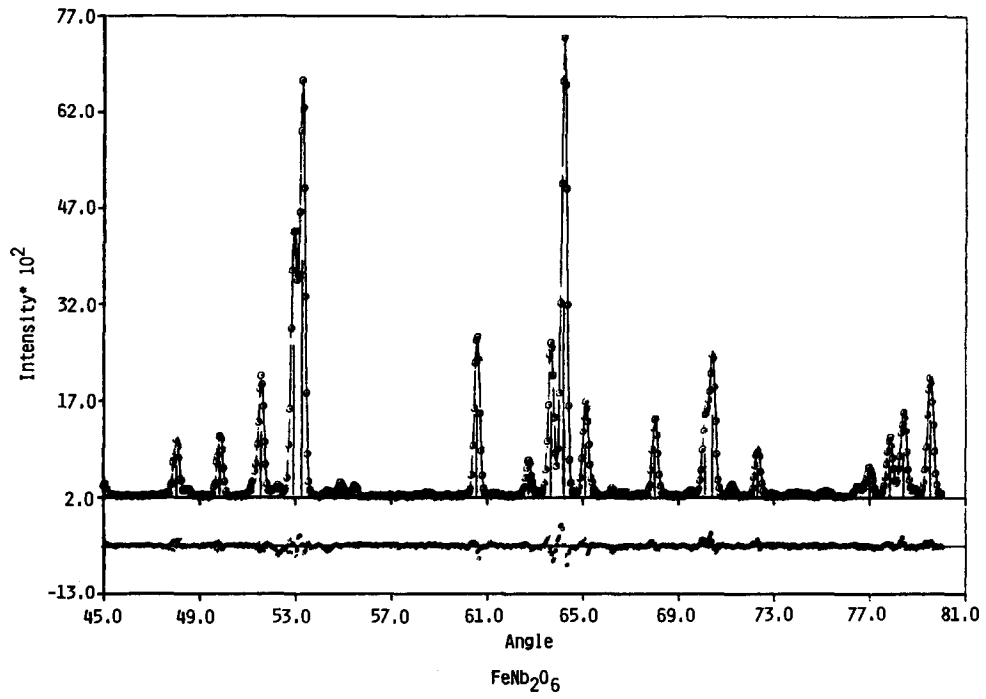


FIG. 3—Continued.

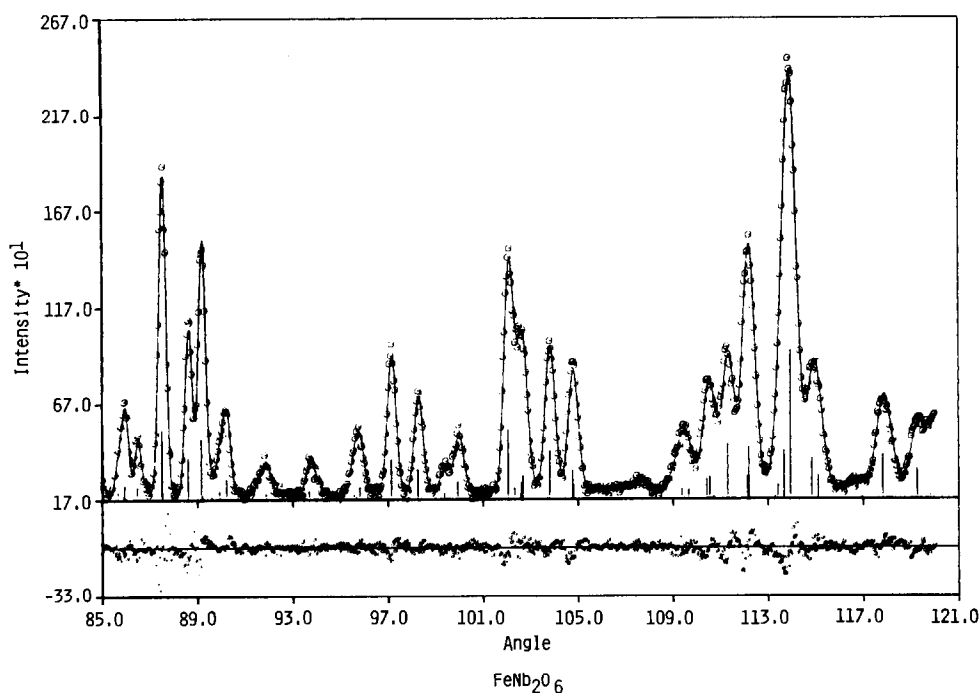


FIG. 3—Continued.

to those described previously for the octahedra and their configuration resembles the distorted fluorite-type structure of the tetragonal phase of ZrO_2 . This structure is isomorphous with those of euxenite (15) and fersmite (16).

$FeNb_2O_6$

Figure 6 shows a projection of the struc-

ture of this compound on the plane (100). If we view the structure along the a axis we see that the zigzag chains characteristic of the α - PbO_2 structure are occupied so that two out of three contain Nb^{5+} ions and one contains Fe^{2+} ions. The relevant interatomic distances are given in Table VII. The octahedron surrounding the Fe^{2+} is quite distorted with an average Fe—O dis-

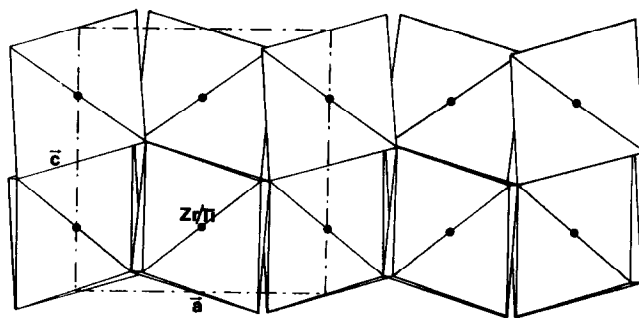


FIG. 4. Projection on (010) of the structure of $ZrTiO_4$. The cations Zr^{4+} and Ti^{4+} occupy positions 4c of space group $Pbcn$. The unit cell of the structure is outlined.

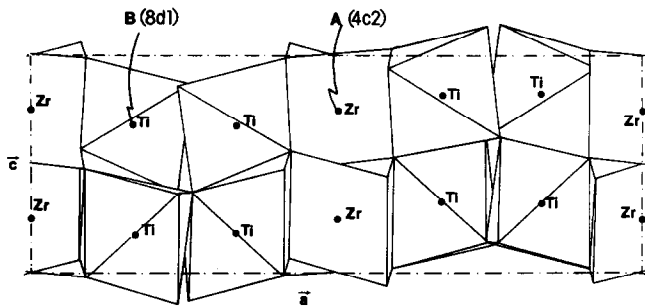


FIG. 5. Projection on the plane (010) of the structure of $Zr_5Ti_7O_{24}$. The sites $4c$ of space group $Pbcn$ are occupied by the Zr^{4+} ions. The sites $8d$ are occupied by $\frac{1}{3} Zr^{4+}$ and $\frac{2}{3} Ti^{4+}$. The unit cell is outlined.

tance of 2.122 Å, while the octahedron around Nb^{5+} is only slightly distorted with an average Nb–O distance of 2.018 Å. These distances are compatible with the ionic radii of O^{2-} , Fe^{2+} , and Nb^{5+} (1.40, 0.75, and 0.64 Å, respectively) (13).

We have applied the second law of Pauling to this structure using the relationship of Brown and Wu (17).

$$s = (R/R_1)^{-N}$$

connecting the bond strength s and the bond length R . The values of the empirical constants R_1 and N are $R_1 = 1.764$ and $N = 5.5$ for iron, and $R_1 = 1.907$ and $N = 5.0$ for niobium. The results obtained are 2.16 for the charge on the iron ion and 4.89 for the charge on the niobium ion. This slight discrepancy on the charges calculated suggests that presence of Fe^{3+} ions in positions

$4c2$ and of ions Nb^{4+} in positions $8d1$. In order to have a charge of 2.16 on the iron sites it is necessary that about 16% of the Fe^{2+} ions are replaced by Fe^{3+} ions. This implies the presence of about 8% of Nb^{4+} ions on the niobium sites. The formula of the compound could then be written



Of course another possible explanation would be that some niobium ions occupy iron sites, but such a configuration is rather unlikely because of the large difference between the valences of the cations involved.

Discussion and Conclusions

The average interatomic distances observed in the structures of the title compounds are summarized in Table VIII. It

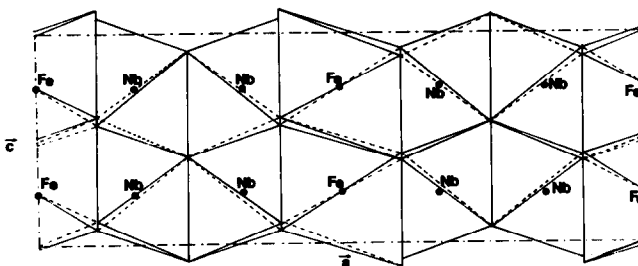


FIG. 6. Projection of the structure of $FeNb_2O_6$ on (010). In this structure the Fe^{2+} and Nb^{5+} ions occupy the $4c$ and $8d$ positions, respectively.

TABLE VII
INTERATOMIC DISTANCES IN THE STRUCTURE OF
 $FeNb_2O_6$

Fe-O		Fe-Fe	
2×	2.093(3)	1×	3.182(2)
2×	2.130(3)		
2×	2.143(3)		
Average 2.122 Å		Fe-Nb	
2×	3.281(3)	1×	3.523(3)
		1×	3.519(3)
Nb-O		Nb-Nb	
1×	1.922(4)	1×	3.267(4)
1×	2.081(3)	1×	3.666(4)
1×	1.800(3)		
1×	2.069(4)		
1×	1.956(3)		
1×	2.277(3)		
Average 2.018 Å			
1×	3.260(4)		
1×	3.324(3)		
O-O (octahedron around Fe ²⁺)		O-O (octahedron around Nb ⁵⁺)	
1×	3.280(4)	1×	2.793(4)
2×	3.111(4)	1×	2.947(4)
1×	2.809(4)	1×	2.888(4)
2×	3.118(4)	1×	2.594(4)
1×	2.809(4)	1×	2.746(4)
1×	2.771(4)	1×	2.867(4)
2×	2.851(4)	1×	2.594(4)
2×	2.855(4)	1×	2.979(4)
Average 2.962 Å		1×	2.904(4)
		1×	2.916(4)
		1×	2.872(4)
		1×	2.895(4)
		Average 2.833 Å	

should be noted that the average distances for the polyhedron around Zr^{4+} in position $4c2$ in the structure of $Zr_5Ti_7O_{24}$ cannot be compared with those obtained for $ZrTiO_4$ and $FeNb_2O_6$ because the polyhedron is a pseudo-cube and not an octahedron. If we consider only the six anions closest to Zr^{4+} , however, the average distances in $Zr_5Ti_7O_{24}$ become $Zr-O = 2.169$ Å and $O-O = 2.957$ Å and these distances are comparable with the corresponding distances in the other two compounds.

As we have pointed out before, the coordination octahedron in $ZrTiO_4$ is very dis-

torted and the cation is considerably displaced with respect to the center. The average distance cation-anion is between those derived from the values of the ionic radii of Ti^{4+} , Zr^{4+} , and O^{2-} . The observed distortion is obviously due to the fact that the octahedron must accommodate cations with very different ionic radii. The situation is different in $FeNb_2O_6$ because Fe^{2+} and Nb^{5+} occupy different sets of positions, and the octahedra around these two cations have different sizes, so that the octahedron around Fe^{2+} is bigger and more deformed than that around the Nb^{5+} ion.

In $Zr_5Ti_7O_{24}$ the difference in the sizes of the coordination polyhedra is considerable because of the large difference between ionic radii. The octahedron formed by the six nearest neighbors of Zr^{4+} (cation A) is very deformed and of a size such that the two second nearest neighbors are located at a distance from the cation only slightly larger than that of the first neighbors. It is then possible to consider the coordination polyhedron as a pseudo-cube rather than an octahedron. The disorder between Ti^{4+} and Zr^{4+} in $Zr_5Ti_7O_{24}$ is possible because the two cations have the same valence. In $FeNb_2O_6$ this condition is not satisfied and no mixing between the cations in positions $4c2$ and $8d1$ is observed. The size of the octahedron surrounding the B cation in $Zr_5Ti_7O_{24}$ is consistent with the value of the distance $Ti^{4+}-O^{2-}$ derived from the radii of these ions.

TABLE VIII
AVERAGE INTERATOMIC DISTANCES IN THE
STRUCTURES OF $ZrTiO_4$, $Zr_5Ti_7O_{24}$, AND $FeNb_2O_6$

	$ZrTiO_4$	$FeNb_2O_6$	$Zr_5Ti_7O_{24}$
Cation-anion dist.	2.079	Fe-O: 2.122	A-O: 2.237
		Nb-O: 2.018	B-O: 1.968
		(O-O) _{Fe} : 2.962	(O-O) _A : 2.638
Anion-anion dist.	2.873	(O-O) _{Nb} : 2.833	(O-O) _B : 2.824

To conclude this discussion we may say that the deformation of the structure of ZrTiO_4 , compared to that of $\alpha\text{-PbO}_2$, is due to the large difference between the sizes of Zr^{4+} and Ti^{4+} . For the two superstructures of $\alpha\text{-PbO}_2$ present in $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ and in FeNb_2O_6 , we may have a structure type fersmite if the difference of ionic radii is large (case of $\text{Zr}_5\text{Ti}_7\text{O}_{24}$) or the structure of columbite if the difference is small (as in FeNb_2O_6).

References

1. R. E. NEWNHAM, *J. Am. Chem. Soc.* **50**, 216 (1967).
2. J. H. STURDIVANT, *Z. Krist.* **75**, 88 (1930).
3. A. E. MCHALE AND R. S. ROTH, *J. Am. Ceram. Soc.* **66**, C-18 (1983).
4. A. C. TURNOCK, *J. Am. Ceram. Soc.* **49**, 177 (1966).
5. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
6. E. PRINCE AND A. SANTORO, Natl. Bur. Stand. US Tech. Note No. 1117, p. 11, 1980.
7. M. M. HALL, V. G. VEERARAGHAVAN, H. RUBIN, AND P. G. WINCHELL, *J. Appl. Crystallogr.* **10**, 66 (1977).
8. E. PRINCE, Natl. Bur. Stand. US Tech. Note No. 1117, p. 8, 1980.
9. G. CAGLIOTI, A. PAOLETTI, AND F. P. RICCI, *Nucl. Instrum.* **3**, 223 (1958).
10. G. E. BACON, *Acta Crystallogr. Sect. A* **28**, 357 (1972).
11. R. O. KEELING, JR., *Acta Crystallogr.* **10**, 209 (1957).
12. R. B. FERGUSON, F. C. HAWTHORNE, AND J. D. GRICE, *Can. Mineral.* **14**, 550 (1976).
13. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
14. G. TEUFER, *Acta Crystallogr.* **15**, 1187 (1962).
15. A. KOMBOV, *Dokl. Akad. Nauk SSSR Earth Sci.* **132**, 597 (1963).
16. J. P. CUMMINGS AND S. H. SIMONSEN, *Am. Mineral.* **55**, 90 (1970).
17. I. D. BROWN AND K. K. WU, *Acta Crystallogr. Sect. B* **32**, 1957 (1976).