JOURNAL OF SOLID STATE CHEMISTRY 35, 167–175 (1980)

Neutron Powder Diffraction Study of the Structures of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$

A. SANTORO, M. MAREZIO,* R. S. ROTH, AND D. MINOR

*National Measurement Laboratory, National Bureau of Standards, Washington, D.C. 20234; and *Laboratoire de Cristallographie, CNRS, 38042 Grenoble Cedex, France*

Received October 24, 1979; in revised form January 7, 1980

The crystal structures of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$ have been refined with the Rietveld method using neutron powder diffraction data collected at room temperature. The results of these refinements show that the coordination of the Ce and Nd cations is 8 with an average Ce–O distance of 2.520 Å in $CeTaO_4$ and 2.480 Å in $CeNbO_4$, and an average Nd–O distance of 2.451 Å in $NdTaO_4$. The Nb and Ta cations in $CeNbO_4$ and $NdTaO_4$ are surrounded by six oxygen ions with Nb–O distances varying between 1.851 and 2.482 Å, and Ta–O distances varying between 1.861 and 2.353 Å. The structural arrangement of $CeTaO_4$ can be regarded as that of an oxidized ABO_3 perovskite. The difference in structure of $CeTaO_4$ and $NdTaO_4$ is most likely due to the difference in size of the rare-earth cations.

Introduction

Of the tantalates and niobates of rare-earth metals only those of Ce^{3+} oxidize in air (*1–4*), and the change of composition is accompanied by changes of the structural and physical properties of the compounds involved. Although the starting oxides have been characterized chemically, little is known about their detailed crystal structures. X-Ray powder and precession patterns have shown (*2*) that $CeTaO_4$ is monoclinic with a $LaTaO_4$-type structure (*5*), while $CeNbO_4$ and $NdTaO_4$ have a fergusonite-like structure which is a monoclinic distortion of scheelite (*2–4*). No refinements of the structures were attempted in these experiments, however, because of the large differences in the X-ray scattering factors of the oxygen and metal atoms.

A detailed knowledge of the structural features of the title compounds is desirable for the understanding of the oxidation mechanisms leading to the formation of the oxygen-rich phases and for conjecturing possible phase relationships between stoichiometric and oxidized materials. Such knowledge can be gained by using neutron diffraction techniques, because the values of the neutron scattering amplitudes of the atoms involved do not differ greatly from one another.

A neutron diffraction study of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$ was therefore undertaken and the results of the analysis are reported in the following sections.

Experimental

The compounds were prepared by mixing the appropriate amounts of tantalum, niobium, cerium, and neodymium oxides and by heating the mixtures overnight at

0022-4596/80/140167-09$02.00/0
Copyright © 1980 by Academic Press, Inc.
All rights of reproduction in any form reserved.

1000°C in platinum crucibles. After they were cooled to room temperature, the products of this heat treatment were ground, heated again at 1400°C for $CeNbO_4$, 1500°C for $CeTaO_4$, and 1600°C for $NdTaO_4$, over a period of 16–20 hr; quenched in water, filtered, and dried. The only single crystals obtained for these materials were too small for neutron diffraction and many of them were twinned, especially in the case of $CeTaO_4$. It was therefore decided to analyze the materials with the powder technique and to refine the structures with the Rietvelt method (*6*).

Neutron diffraction measurements were made at room temperature on a powder diffractometer at the National Bureau of Standards Reactor, using the experimental conditions shown in Table I. As a general procedure, the contribution to the profile from the background is determined at portions of the powder pattern free from diffraction effects, and estimated by extrapolation from these regions to those where overlapping is more severe. The reliability of this procedure depends on the materials under study and on the adopted experimental conditions. In our case the distribution of the reflections and the resolution of the diffractometer used for the intensity measurements leave many regions of the powder patterns free from diffracted intensity over the entire 2θ angular intervals considered. This is a favorable circumstance, as the reliability with which thermal parameters are determined is strongly dependent on the evaluation of background. The structural refinements were based on space group $P2_1/c$ for $CeTaO_4$ and $I2/a$[1] for $CeNbO_4$ and $NdTaO_4$. The neutron scattering amplitudes used were $b(\mathrm{Ta}) = 0.70$, $b(\mathrm{Ce}) = 0.48$, $b(\mathrm{Nb}) = 0.71$, $b(\mathrm{Nd}) = 0.72$, and $b(0) = 0.58 \times 10^{-12}$ cm (*7*). The initial values of the structural parameters were those obtained in the X-ray study of $LaTaO_4$ (*5*) for $CeTaO_4$ and those obtained in the X-ray study of $YNbO_4$ (*8*) for $CeNbO_4$ and $NdTaO_4$. In all cases individual isotropic temperature factors were used in the calculations and were allowed to vary. The starting lattice constants were determined with the X-ray powder method and the initial values of the profile parameters U, V, and W were calculated theoretically (*9*). The total number of refined structural, lattice, and profile parameters was 33 for $CeTaO_4$ and 21 for $CeNbO_4$ and $NdTaO_4$. Refinement was continued until all shifts were less than 0.3σ.

TABLE I

EXPERIMENTAL CONDITIONS USED TO COLLECT THE POWDER INTENSITY DATA FOR $CeTaO_4$, $CeNbO_4$, AND $NdTaO_4$

Monochromatic beam: reflection 220 of a Cu monochromator in transmission geometry.
Mean neutron wavelength: 1.5416(3) Å
Horizontal divergences[a]
(i) In-pile collimator: 10-min arc;
(ii) Monochromatic beam collimator: 20-min arc;
(iii) Diffracted beam collimator: 10-min arc.
Monochromator mosaic spread:[a] 15-min arc.
Sample container: V can of 1-cm diameter.

---

[a] For a definition of these quantities see Caglioti *et al.* (*9*).

From the early stages of the analysis it was apparent that the isotropic temperature factor of the Nd atom in the structure of $NdTaO_4$ was converging to an impossible value [$b(\mathrm{Nd}) = -0.19$ Å^2]. Such abnormal behavior of the thermal parameter may be caused by the use of an improper neutron scattering amplitude for the Nd atom, and, in fact, a check of the literature revealed that the value $b(\mathrm{Nd}) = 0.72 \times 10^{-12}$ cm used in the calculations was too low. More reasonable results and lower R factors were obtained by using an updated amplitude of 0.77×10^{-12} cm (*10*), but $b(\mathrm{Nd})$ still converged to an implausibly low value (0.13 Å^2). At this point $b(\mathrm{Nd})$ was allowed to

---

[1] The standard setting for space group $I2/a$ is $C2/c$. The transformation matrix from our axes to the conventional ones is $(00\bar{1}/010/101)$.

TABLE II

COHERENT NEUTRON SCATTERING AMPLITUDE OF Nd

b(Nd)	0.72[a]	0.77[b]	0.80[c]
B(Nd)	−0.19(4) Å^2	0.13(4)	0.31(4)
B(Ta)	0.70(5)	0.57(5)	0.50(5)
B(O1)	0.67(4)	0.52(4)	0.43(4)
B(O2)	0.71(4)	0.58(4)	0.51(4)
R[d]	5.41	5.23	5.24
R_p	9.76	9.41	9.42
R_w	11.07	10.73	10.70
R_e	7.08	7.06	7.06
χ	1.57	1.52	1.52

[a] Reference (*7*).

[b] Reference (*10*).

[c] From refinement of $NdTaO_4$.

[d] $$R = 100 \times \left\{\frac{\Sigma|I(\mathrm{obs}) - I(\mathrm{cal})|}{\Sigma I(\mathrm{obs})}\right\},$$

$$R_p = 100 \times \left\{\frac{\Sigma|y(\mathrm{obs}) - y(\mathrm{cal})|}{\Sigma y(\mathrm{obs})}\right\},$$

$$R_w = 100 \times \left\{\frac{\Sigma w[y(\mathrm{obs}) - y(\mathrm{cal})]^2}{\Sigma w[y(\mathrm{obs})]^2}\right\}^{1/2},$$

$$R_e = 100 \times \left\{\frac{N - P + C}{\Sigma w[y(\mathrm{obs})]^2}\right\}^{1/2}.$$

In the above formulas N is the number of statistically independent observations, P the number of parameters refined, C the number of constraints, I the integrated intensities, and y the profile intensities of weight w.

vary. Although correlation between the scattering amplitude and the temperature factor was large (78%), the refinement proceeded to a stable minimum. A final value $b(\mathrm{Nd}) = 0.80\ (1) \times 10^{-12}$ cm was obtained with reasonable thermal parameters for all atoms in the structure. The results of these calculations are summarized in Table II. (It is worth noting that the atomic positional parameters obtained in the three refinements of the structure did not vary by more than two times the standard deviation.)

Refinements of the structures of $CeNbO_4$ and $NdTaO_4$ in the centric space group $I2/a$ were satisfactory; therefore, the centric space group was assumed for the two compounds.

Recently, Sakata and Cooper (*11*) concluded that in the Rietveld method the observations are incorrectly weighted and the estimated standard deviations are smaller by a factor of 2 or more than those obtained in a refinement based on integrated intensities. These conclusions, however, do not seem to be justified. As pointed out by Prince (*12*), the high precision of the profile method is a consequence of the fact that in this method each peak is assumed to be Gaussian, so that each data point becomes an independent measurement of the same intensity. This results in a more precise estimate of the intensity. In what follows, therefore, we quote the estimated standard deviations obtained in the profile refinement.

Results

(*a*) *Profile Parameters*

The profile parameters obtained in the refinements are shown in Table III, where they are compared with those calculated theoretically. The experimental values agree closely with one another and with those of other compounds studied with the same experimental conditions, but they are significantly higher than the theoretical values. Discrepancies of this kind have been

TABLE III

PROFILE PARAMETERS

	U	V	W (deg^2)
Calculated	0.212	−0.231	0.107
$CeTaO_4$	0.43(2)	−0.47(2)	0.221(6)
$CeNbO_4$	0.418(8)	−0.47(1)	0.219(3)
$NdTaO_4$	0.39(1)	−0.45(2)	0.221(5)

Note. The parameters U, V, and W appear in the equation $H^2 = U \tan^2\theta + V \tan\theta + W$, where H is the full width at half maximum of a reflection occurring at the Bragg angle θ. The theoretical values of U, V, and W have been calculated with the expressions derived by Caglioti *et al.* (*9*).

TABLE IV

LATTICE PARAMETERS

	$CeTaO_4$	$NdTaO_4$	$CeNbO_4$
a			
Neutrons	7.6161(3)	5.5115(2)	5.5350(1)
X rays	7.618(1)	5.520(1)	5.542(1)
b			
Neutrons	5.5254(2)	11.2320(3)	11.3991(3)
X rays	5.531(1)	11.244(2)	11.414(1)
c			
Neutrons	7.7588(3)	5.1112(1)	5.1590(1)
X rays	7.767(1)	5.117(1)	5.165(1)
β			
Neutrons	100.87(2)	95.71(1)	94.60(1)
X rays	100.94(2)	95.72(1)	94.60(1)

Note. The errors on the cell dimensions determined by neutron diffraction do not include the error in the neutron wavelength.

noted previously (*13*, *14*) and are probably caused by approximations made in deriving the original theory rather than by crystallite size effects or structural distortions.

(*b*) *Lattice Parameters*

The lattice constants obtained in the neutron study agree well with those determined with the X-ray powder method. The former, however, are systematically smaller than the latter, as shown in Table IV. This effect is probably the result of underestimating the neutron wavelength of about 1 part in 1000. Clearly, the standard deviation quoted in Table I has to be considered a measure of precision, rather than one of accuracy. The X-ray parameters, therefore, should be preferred over those obtained in the neutron refinement, and, in fact, these parameters were used in the calculation of the interatomic distances so that none of the conclusions discussed in the paper is affected by the error on the wavelength.

(*c*) *Structure of $CeTaO_4$*

The results of the structure refinement of $CeTaO_4$ are shown in Table V. A projection of the unit cell on the (010) plane is shown in Fig. 1 and cation–oxygen distances are given in Table VI. In the asymmetric unit there are one type of tantalum and one type of cerium cation, whereas there are four

TABLE V

RESULTS OF THE TOTAL PROFILE REFINEMENT OF THE STRUCTURE OF $CeTaO_4$[a,b]

Atom	Position	X	Y	Z	B
Ce	4*e*1	0.3441(6)	0.7728(7)	0.0999(5)	0.73(8)
Ta	4*e*1	0.1668(4)	0.2670(6)	0.3045(4)	0.65(6)
O(1)	4*e*1	0.1680(5)	0.1604(6)	0.0544(5)	0.69(8)
O(2)	4*e*1	0.0568(5)	0.5869(5)	0.2067(5)	0.90(8)
O(3)	4*e*1	0.3823(4)	0.4842(6)	0.3312(5)	0.52(7)
O(4)	4*e*1	0.3338(4)	0.0084(6)	0.3671(4)	0.78(6)

$R = 3.82$, $R_p = 8.29$, $R_w = 10.04$; $R_e = 8.08$.
Number of points above background: 1277.
$2\Theta(\text{initial}) = 11.0°$, $2\Theta(\text{final}) = 94°$, step = 0.05°.
Number of independent Bragg reflections: 290.
Parameters refined
(i) Structural (including scale factor) = 25,
(ii) Lattice (including zero point for 2Θ) = 5,
(iii) Profile = 3.

---

[a] Figures in parentheses are standard deviations in the last decimal figure.

[b] Space group $P2_1/c$.

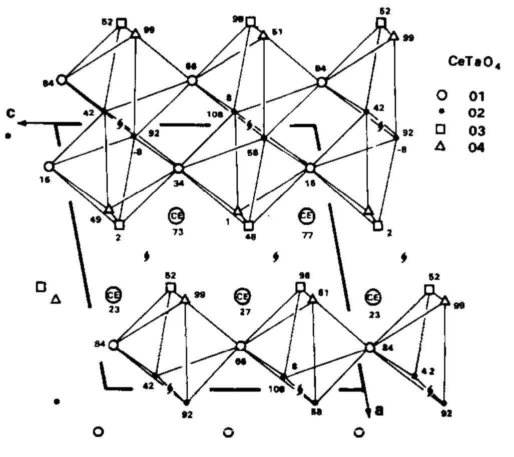

FIG. 1. Projection on (010) of the structure of CeTaO$_4$. The Ta cations are located at the centers of the distorted octahedra outlined in the figure. The y coordinate (× 100) is given for each atom.

types of oxygen anion. The tantalum cations are located at the centers of the oxygen octahedra which are outlined in Fig. 1. Each octahedron is formed by two oxygen atoms of type O(1), two of type O(2), one of type O(3), and one of type O(4). The average Ta–O distance is 1.990 Å. The octahedra share only vertices among themselves; they form slabs which are infinite in two dimensions (along the b and c axes) and are two octahedra thick in the third (the a^* axis). These are actually perovskite-like slabs and the cerium atoms are located in sites similar to the A sites of the ABO_3 perovskite structure. The cerium cations are surrounded by eleven oxygen anions, belonging to the same slab [three O(1), four O(2), two O(3), and two O(4)]. The twelfth is replaced by two oxygen anions of the adjacent slab. These two come closer to the cerium cation because each slab is displaced with respect to the adjacent one by half the height of an octahedron. The slabs are linked together by these interslab Ce–O bonds. In order to form these bonds, the cerium cations move out of the centers of the 11-oxygen polyhedra. As a result, the polyhedra become so distorted that only six oxygen anions are nearest neighbors to the cerium cation. The Ce–O distances corresponding to the interslab bonds (2.361 and 2.826 Å) are of the same order of magnitude as those of the intraslab Ce–O bonds. Each cerium cation is bonded to one O(1), one O(2), three O(3), and three O(4) oxygen atoms. The coordination number of the cerium cations is thus 8, and the average Ce–O distance is 2.520 Å. The coordination number of the oxygen anions is 3 for O(1) and O(2) and 4 for O(3) and O(4). The first two are bonded to two Ta and one Ce cations, whereas the other two are bonded to one Ta and three Ce cations. If one calculates the charge of these four oxygen anions without taking into account the differences in the anion–cation distances (anionic charge = $\Sigma_i S_i$, where S_i, the bond strength, is the ratio Z/n, Z is the cationic charge, and n the cationic coordination number), one finds for O(1) and O(2), $\Sigma_i S_i$ = 2.04 and for O(3) and O(4), $\Sigma_i S_i$ = 1.96.

TABLE VI

CATION–OXYGEN DISTANCES (Å) IN CeTaO$_4$

Tantalum–octahedron	
Ta–O(1)	2.032(5)
O(1)	1.980(5)
O(2)	2.041(4)
O(2)	1.960(5)
O(3)	2.013(4)
O(4)	1.914(5)
Average = 1.990	
Cerium–polyhedron	
Ce–O(1)	2.518(5)
O(2)	2.688(6)
O(3)	2.380(5)
O(3)	2.361(5)[a]
O(3)	2.545(6)
O(4)	2.464(5)
O(4)	2.826(6)[a]
O(4)	2.375(5)
Average = 2.520	

[a] These are interblocks Ce–O distances.

These values indicate that only a small part of the distortion is needed to balance the electrostatic charge.

It was pointed out recently (*1, 2*) that $CeTaO_4$ can absorb oxygen according to the oxidation–reduction reaction

$$CeTaO_4 + 1/2O_2 \rightarrow Ce^{3+}_{1-2x}Ce^{4+}_{2x}TaO_{4+x}.$$

The x parameter is variable and temperature dependent. Three distinct ranges in x ($x \simeq 0.49, x \simeq 0.37, x \simeq 0.12$) were found to yield three different phases.

The structural arrangment of $CeTaO_4$ can also be regarded as that of an oxidized ABO_3 perovskite. An extra oxygen layer is inserted in the structure every three anion layers, and this causes the separation of the perovskite blocks into finite two-octahedron-thick slabs. For instance, it can be seen from Fig. 1 that if the oxygen anions O(3) at $y = 1.02$ were coincident with O(4) at $y = 0.99$, and if O(4) at $y = 0.49$ were coincident with O(3) at $y = 0.52$, the structural arrangement would be truly an ABO_3 perovskite-like arrangement. When these oxygen anions are not coincident, the ABO_4 compound is obtained instead.

(*d*) *Structures of $CeNbO_4$ and $NdTaO_4$*

The results of the profile refinements of $CeNbO_4$ and $NdTaO_4$ are given in Tables VII and VIII and relevant cation–oxygen distances in Tables IX and X. The two compounds are isostructural and, therefore, many of the considerations made for $CeNbO_4$ also apply to $NdTaO_4$. Figure 2 shows the arrangement of cerium and niobium polyhedra in $CeNbO_4$, as viewed down the monoclinic *b* axis. This structure is a monoclinic distortion of the tetragonal structure of scheelite, $CaWO_4$.

There are on cerium, one niobium, and two oxygen ions in the asymmetric unit. The cations have a distorted, face-centered cubic arrangement. The cerium cations are surrounded by eight oxygen ions, four O(1) and four O(2), forming two interpenetrated tetrahedra. The average Ce–O distance is 2.480 Å. The niobium cations are surrounded by four close oxygen ions, two O(1) and two O(2), arranged as a distorted tetrahedron. The average Nb–O distance over these four neighbors is 1.886 Å. There are four other oxygen ions around the niobium cations, each one capping a face of the closest tetrahedron. Two

TABLE VII

RESULTS OF THE TOTAL PROFILE REFINEMENT OF THE STRUCTURE OF $CeNbO_4$[a]

Atom	Position	*X*	*Y*	*Z*	*B*
Ce	4*e*2	$\frac{1}{4}$	0.1202(2)	0	0.41(5)
Nb	4*e*2	$\frac{1}{4}$	0.6470(1)	0	0.40(4)
O(1)	8*f*1	0.0129(3)	0.7171(1)	0.2031(3)	0.68(3)
O(2)	8*f*1	0.8999(3)	0.4553(1)	0.2399(3)	0.60(3)

$R = 3.32$, $R_p = 7.33$, $R_w = 8.94$, $R_e = 6.34$.
Number of points above background: 1520
2Θ(initial) = 14.5°, 2Θ(final) = 111.7°, step = 0.05°.
Number of independent Bragg reflections: 212.
Parameters refined
(i) Structural (including scale factor) = 13,
(ii) Lattice (including zero point for 2Θ) = 5,
(iii) Profile = 3.

[a] Space Group *I*2/*a*.

TABLE VIII

RESULTS OF THE TOTAL PROFILE REFINEMENT OF THE STRUCTURE OF $NdTaO_4$[a]

Atom	Position	X	Y	Z	B
Nd	$4e2$	$\frac{1}{4}$	0.1178(2)	0	0.31(4)
Ta	$4e2$	$\frac{1}{4}$	0.6515(2)	0	0.50(5)
O(1)	$8f1$	0.0152(4)	0.7188(2)	0.2165(5)	0.43(4)
O(2)	$8f1$	0.9014(4)	0.4563(2)	0.2396(4)	0.51(4)

$R = 5.24$, $R_p = 9.42$, $R_w = 10.70$, $R_e = 7.06$.
Number of points above background: 1516.
2Θ(initial) = 15.0°, 2Θ(final) = 114.5°, step = 0.05°.
Number of independent Bragg reflections: 220.
Parameters refined:
(i) Structural (including scale factor) = 13,
(ii) Lattice (including zero point for 2Θ) = 5,
(iii) Profile = 3.

[a] Space group $I2/a$.

of these oxygen ions are close enough (the corresponding Nb–O distance being 2.482 Å) that they may be considered bonded to the niobium atoms, whereas the other two are removed much farther and cannot be considered as involved in the bonds. In the scheelite $CaWO_4$ structure, the eight oxygen ions surrounding the tungsten cation are arranged as two interpenetrated tetrahedra of very different sizes. The two sets of W–O distances are 1.78 and 2.91 Å (*15*). The calcium cations are also surrounded by eight oxygen ions but differ from the tungsten cations because the two sets of cation–oxygen distances in the calcium case are very close, 2.44 and 2.48 Å.

One possible way of looking at the scheelite structure is to consider it as a distorted superstructure of fluorite, CaF_2. The fluorite structure contains a simple cubic array of anions so that all cations which form a perfect face-centered cubic lattice have an eightfold coordination. In the scheelite structure, the cations are considerably distorted from the fcc lattice and the anions move away from the simple

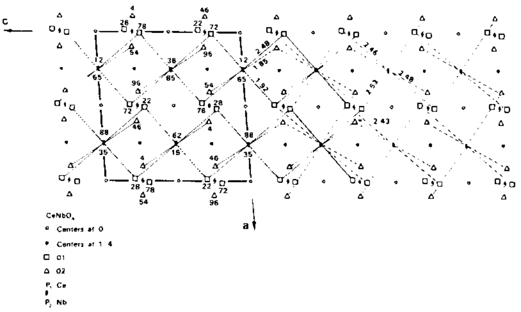

FIG. 2. Projection of (010) of the structure of $CeNbO_4$. The solid lines identify the Nb polyhedron, the broken lines the Ce polyhedron. The y coordinate (×100) is indicated for each atom. The relevant Ce–O and Nb–O distances are also given.

TABLE IX

CATION–OXYGEN DISTANCES (Å) IN $CeNbO_4$

Cerium polyhedron	
Ce–O(1) ×2	2.461(2)
O(1) ×2	2.535(2)
O(2) ×2	2.428(2)
O(2) ×2	2.494(2)
Average = 2.480	
Niobium polyhedron	
Nb–O(1) ×2	1.920(2)
O(2) ×2	1.851(2)
O(1) ×2	2.482(2)
Average = 2.084	

TABLE X

CATION–OXYGEN DISTANCES (Å) IN $NdTaO_4$

Neodymium polyhedron	
Nd–O(1) ×2	2.441(3)
O(1) ×2	2.534(3)
O(2) ×2	2.380(2)
O(2) ×2	2.449(3)
Average = 2.451	
Tantalum polyhedron	
Ta–O(1) ×2	1.941(2)
O(2) ×2	1.861(3)
O(1) ×2	2.353(3)
Average = 2.052	

cubic positions in the following manner: four of the eight anions around the positions occupied by the small cations move closer to these cations and in this way a tetrahedral coordination is achieved for the small cations. The remaining four anions move farther away from these cations in such a way that the large cations still have an eightfold coordination. The resulting polyhedron around the large cations has *mm* symmetry, i.e., lower than the *m*3*m* symmetry of the cubic structure. From this point of view the fergusonite-like structures could be considered as intermediate between the fluorite and the scheelite structures, even though the fluorite is cubic, the scheelite is tetragonal, and the fergusonite-like structures have monoclinic symmetry. In the latter type of structure, two anions of the four forming the larger tetrahedron around the small pentavalent cations, come closer to Nb^{5+} cations in $CeNbO_4$ and to the Ta^{5+} cations in $NdTaO_4$. It should also be pointed out that in the scheelite structure the cubic arrangement of the anions is so distorted that it is better described as a puckered hexagonal network.

In the structure of $CeNbO_4$, the oxygen atom O(1) is surrounded by two niobium and two cerium atoms and the O(2) atom is surrounded by one niobium and two cerium atoms. Consequently, if one does not take into account the individual distances, the former anion is overbonded ($\Sigma_i S_i = 2.42$), whereas the latter one is underbonded ($\Sigma_i S_i = 1.58$). Therefore, in this structure the differences in these distances are mainly due to balancing the electrostatic charge.

As we mentioned earlier, $NdTaO_4$ and $CeNbO_4$ are isostructural. A difference which is worthwhile to point out lies in the coordination of the pentavalent cations. As can be seen from Tables IX and X the first two sets of M^{5+}–O distances increase (from 1.851 and 1.920 to 1.861 and 1.941 Å), whereas the third set decreases (from 2.482 to 2.353 Å) on going from the niobate to the tantalate. These values indicate that the oxygen atoms in this third set behave, at least in the niobate, as second-nearest neighbors. Therefore the coordination number of these cations should be taken as 4 + 2, although the Ta^{5+} ion appears to be approaching sixfold coordination.

The change in structure which takes place in the tantalum series is probably due to the size of the rare-earth cation. When this size becomes too large for the *A* site of the fergusonite-like structure, the tantalates crystallize with the $LaTaO_4$-type structure. The same structural change does not take place in the niobates because of the preference of the Nb^{5+} cations for a coordination smaller than 6.

References

1. T. NEGAS, R. S. ROTH, C. L. MCDANIEL, H. S. PARKER, AND C. D. OLSON, *Mater. Res. Bull.* **12,** 1161 (1977).
2. R. S. ROTH, T. NEGAS, H. S. PARKER, D. B. MINOR, AND C. JONES, *Mater. Res. Bull.* **12,** 1173 (1977).
3. R. S. ROTH, T. NEGAS, H. S. PARKER, D. B. MINOR, C. D. OLSON, AND C. SKARDA, *in* "The Rare Earths in Modern Science and Technology" (G. J. McCarthy and J. J. Rhyne, Eds.), p. 163, Plenum, New York/London (1978).
4. R. J. CAVA, T. NEGAS, R. S. ROTH, H. S. PARKER, D. B. MINOR AND C. D. OLSON, *in* "The Rare

Earths in Modern Science and Technology" (G. J. McCarthy and J. J. Rhyne, Eds.), p. 181, Plenum, New York/London (1978).

5. T. A. Kirova and V. B. Alexandrov, *Dokl. Akad. Nauk USSR* **201**, 1095 (1971).
6. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
7. G. E. Bacon, *Acta Crystallogr. A* **28**, 357 (1972).
8. C. T. Prewitt, private communication.
9. G. Caglioti, A. Paoletti, and F. P. Ricci, *Nucl. Instrum.* **3**, 223 (1958).
10. W. B. Yelon, *Neutron Diffraction Newsletter* (1977).
11. M. Sakata and M. J. Cooper, MPD/NBS/95 AERE, Harwell, July 1978.
12. E. Prince, submitted for publication.
13. G. Caglioti and F. P. Ricci, *Nucl. Instrum. Methods* **15**, 155 (1962).
14. A. Santoro, R. S. Roth, and D. B. Minor, *Acta Crystallogr. B* **33**, 3945 (1977).
15. A. Zalkin and D. H. Templeton, *J. Chem. Phys.* **40**, 501 (1964).