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The Crystal Structure of $Na_3Nb_{12}O_{31}F$ Determined by HREM and Image Processing

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A new type of GTB-like structure of $Na_3Nb_{12}O_{31}F$ has been studied by high-resolution electron microscopy (HREM) in combination with computerized image processing. The structure of $Na_3Nb_{12}O_{31}F$ is tetragonal (space group $P4$) with $a = b = 1.749$ and $c = 0.3944$ nm. The coordinates of the Nb atoms obtained by HREM and image processing agreed with the coordinates from an X-ray diffraction study within 0.013 nm.

Introduction

High-resolution electron microscopy (HREM) has been applied with great success to the studies of inorganic materials (*1–6*) and computerized image processing of electron micrographs has been widely used for three-dimensional structure determination of biological macromolecules (*7*, *8*). Klug (*9*) suggested that image processing could also be applied to electron micrographs of inorganic crystals. Recently, Hovmöller *et al.* (*10*) have determined the atomic coordinates (in projection) of metal atoms in a thin crystal of $K_{8-x}Nb_{16-x}W_{12+x}O_{80}$ (where $x \simeq 1$) by HREM in combination with computerized image processing, to an accuracy of 0.01 nm. With the present study we show again that an accuracy of about 0.01 nm can be achieved by this method.

Structure Determination by HREM and Image Processing

Samples of the title compound were prepared by heating well-ground mixtures of NaF and Nb_2O_5 in proportions close to 1 : 8. The reaction was carried out in a sealed platinum capsule at 1200°C for 3 days and then quenched in water. Guinier X-ray powder patterns of the sample indicated the presence of N–Nb_2O_5 and a hitherto unknown phase, which could also be distinguished by different colors. The structure of the new oxide, $Na_3Nb_{12}O_{31}F$, was determined by single crystal X-ray diffraction analysis (*11*).

High-resolution electron microscopy images were taken in a JEM 200CX electron microscope equipped with a top-entry ultrahigh-resolution goniometer, the C_s of the pole pieces being 1.2 mm with a point reso-

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lution of 0.26 nm. Since numerous factors can adversely affect the quality of these micrographs, it is necessary to evaluate and select the best image by optical diffraction. The values of defocus can be determined by the position of the dark rings in the optical diffraction pattern, and the amplitudes and phases of the Fourier components of the structure can then be corrected using the calculated values of the contrast transfer function. The degree of astigmatism presented in the electron micrograph can be determined from the ellipticity of the rings in the optical diffraction pattern. A number of electron micrographs taken at different defocus values and different regions of crystal were examined in the optical diffractometer, and a nonastigmatic micrograph which had been recorded at Scherzer focus, with a magnification of 690,000 times, was selected for further analysis.

One thin area of the crystal showed a homogeneous local average optical density as well as a constant optical diffraction pattern, indicating that the variation in thickness, structure, and orientation was very small. This region of the electron micrograph was selected for further analysis by image processing. A region equal to about 72 unit cells was digitized using a Joyce–Loebl microdensitometer MDM6. Points (256 × 256) were scanned with a sampling aperture size of 40 × 40 μm. Figure 1 shows a high-resolution image of the new oxide projected along [001]. The scanned area is outlined by white lines. At a magnification of 690,000 times, a 40 × 40-μm sampling corresponds to an area of 0.58 × 0.58 Å^2. Such sampling preserves the details of the structure to at least 2.3 Å resolution. The information in the electron micrograph was transferred in digital form to a VAX 11/750 computer, on which all further processing was performed.

The Fourier transform of the digitized image was first calculated, as a matrix of

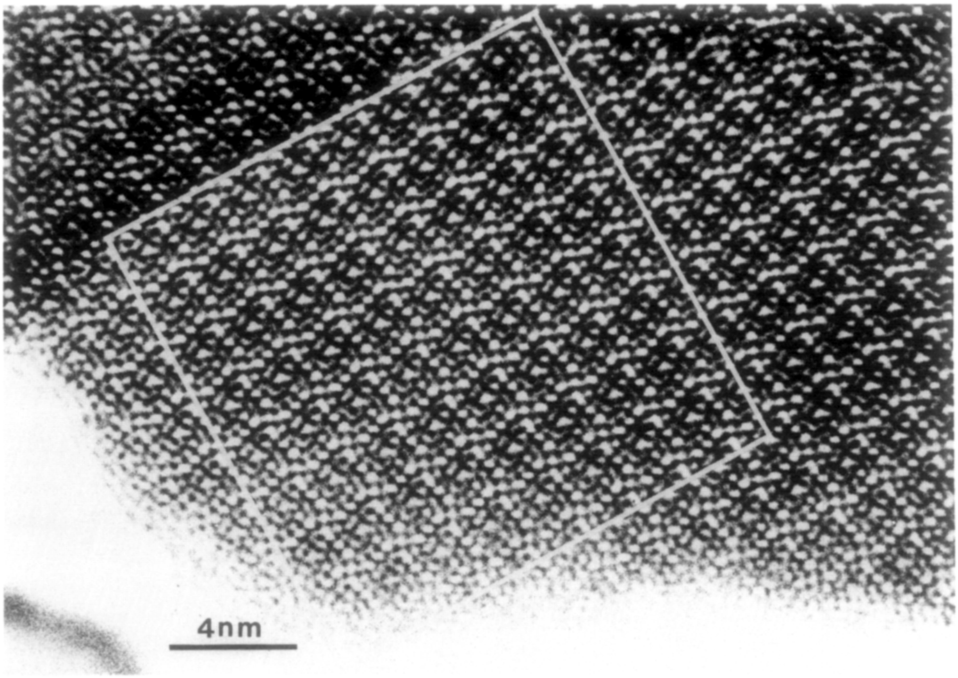

FIG. 1. Structure image of $Na_3Nb_{12}O_{31}F$, viewed along [001]. Scanned area is outlined.

TABLE I

THE VALUES OF THE AMPLITUDES AND PHASES FOR ALL REFLECTIONS IN THE UNIQUE HALF OF THE DIFFRACTION PATTERN WITHIN A RESOLUTION OF 2.5 Å

			*P*1 symmetry		*P*4 symmetry	
h	*k*	*l*	Ampl.	Phase	Ampl.	Phase
0	−7	0	485	262	338	180
7	0	0	191	−164	338	180
1	−7	0	186	259	114	180
7	1	0	42	−185	114	180
2	−7	0	293	75	188	180
7	2	0	82	−201	188	180
3	−7	0	554	211	343	180
7	3	0	131	−340	343	180
4	−7	0	134	63	82	0
7	4	0	29	−340	82	0
5	−7	0	43	39	62	0
7	5	0	81	22	62	0
0	−6	0	1460	38	1261	0
6	0	0	1062	−291	1261	0
1	−6	0	371	323	283	0
6	1	0	194	−279	283	0
2	−6	0	2259	44	1443	0
6	2	0	627	−115	1443	0
3	−6	0	329	22	233	0
6	3	0	136	−52	233	0
4	−6	0	854	41	487	0
6	4	0	119	−175	487	0
5	−6	0	240	267	164	0
6	5	0	88	−40	164	0
6	−6	0	236	291	148	180
6	6	0	60	−142	148	180
0	−5	0	1904	34	1529	0
5	0	0	1154	7	1529	0
1	−5	0	3670	347	2903	0
5	1	0	2135	−324	2903	0
2	−5	0	623	100	472	180
5	2	0	320	−131	472	180
3	−5	0	1742	224	1472	0
5	3	0	1201	−347	1472	0
4	−5	0	821	219	524	180
5	4	0	227	−35	524	180
5	−5	0	324	312	162	0
5	5	0	−18	−42	162	0
6	−5	0	236	331	180	0
5	6	0	124	−279	180	0
0	−4	0	4444	355	3396	0
4	0	0	2347	−4	3396	0
1	−4	0	4476	160	3362	180
4	1	0	2247	−181	3362	180
2	−4	0	6155	322	4747	0
4	2	0	3338	−351	4747	0
3	−4	0	1484	351	1091	0
4	3	0	698	−356	1091	0
4	−4	0	389	223	542	180
4	4	0	695	−210	542	180
5	−4	0	436	209	264	180
4	5	0	92	−133	264	180
6	−4	0	299	82	150	0
4	6	0	−22	−177	150	0
7	−4	0	142	−33	109	0
4	7	0	75	−218	109	0
0	−3	0	760	205	1163	180
3	0	0	1566	146	1163	180
1	−3	0	3031	315	2502	0
3	1	0	1983	1	2502	0
2	−3	0	1535	165	1459	180
3	2	0	1382	−155	1459	180
3	−3	0	238	292	479	0
3	3	0	719	−23	479	0
4	−3	0	2718	171	2266	180
3	4	0	1813	−214	2266	180
5	−3	0	2128	206	2259	180
3	5	0	2389	−244	2259	180
6	−3	0	319	−16	279	0
3	6	0	239	−134	279	0
7	−3	0	297	119	149	180
3	7	0	0	−296	149	180
0	−2	0	1941	306	2105	0
2	0	0	2269	−5	2105	0
1	−2	0	576	328	752	180
2	1	0	928	−178	752	180
2	−2	0	1318	296	854	0
2	2	0	390	−106	854	0
3	−2	0	2798	323	2607	0
2	3	0	2416	7	2607	0
4	−2	0	5810	−10	5647	0
2	4	0	5483	−24	5647	0
5	−2	0	1200	189	1178	180
2	5	0	1154	−228	1178	180
6	−2	0	1276	−120	1204	180
2	6	0	1132	−262	1204	180
7	−2	0	138	135	148	180
2	7	0	158	−230	148	180
0	−1	0	4085	168	3429	180
1	0	0	2773	150	3429	180
1	−1	0	1749	346	1398	0
1	1	0	1047	−30	1398	0
2	−1	0	6138	326	6043	0
1	2	0	5948	5	6043	0

TABLE I—*Continued*

			$P1$ symmetry		$P4$ symmetry	
h	k	l	Ampl.	Phase	Ampl.	Phase
3	−1	0	2349	142	2246	180
1	3	0	2142	−193	2246	180
4	−1	0	1439	−2	1720	0
1	4	0	2001	−14	1720	0
5	−1	0	3530	−157	4523	180
1	5	0	5515	−215	4523	180
6	−1	0	333	108	607	0
1	6	0	880	−56	607	0
7	−1	0	32	−93	157	180
1	7	0	282	−132	157	180

256×256 complex numbers $(A + iB)$. This contains the information of both amplitude and phase. Amplitudes $(\sqrt{A^2 + B^2})$ were determined by integrating over the 3×3 points closest to the predicted position of the lattice point in the Fourier transform followed by subtraction of the local background. The phase value (= arc tan B/A ($+180°$ for $A < 0°$)) was read off in the Fourier transform at the point closest to the predicted position of the lattice point. The result was a list of numbers (h, k, Ampl., Phase) for all 102 reflections in the unique half of the diffraction pattern within a resolution of 2.5 Å (Table I). The amplitude part of the complex number of the Fourier transform was also displayed on a digital VS11 raster graphics system (Fig. 2b).

The space group of the crystal is $P4$ (*11*). The effects of symmetry on the amplitudes and phases of the diffraction points are the following: the amplitudes show 4 symmetry, that is $|F(hkl)| = |F(\bar{k}hl)| = |F(\bar{h}\bar{k}l)| = |F(k\bar{h}l)|$. All reflections in a centrosymmetric projection have phase restriction, being either 0 or 180°, provided the origin is on a twofold (or fourfold) axis.

Initially, the phases of the computed Fourier transform of the digitized image have arbitrary values because the phase origin is inferred from the starting position of the densitometer and is unlikely to superpose on this fourfold axis. A computer program moves the position of the origin stepwise along both a and b to a total of 120×120 evenly spaced points within the unit cell. For each of these positions, the smallest deviation from 0 or 180° is calculated for

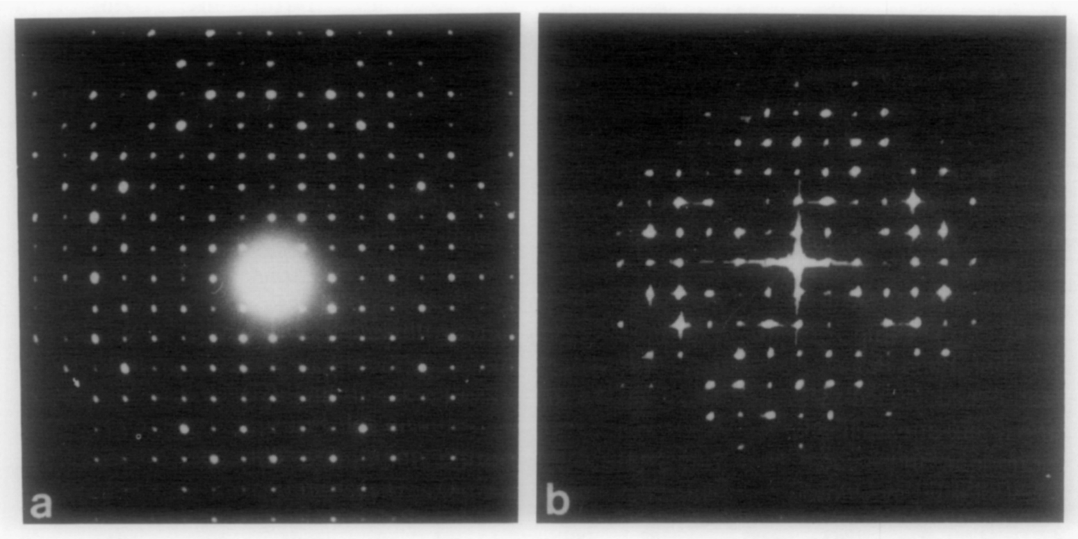

FIG. 2. (a) Electron diffraction pattern [001] of $Na_3Nb_{12}O_{31}F$. (b) Calculated amplitude of the diffraction pattern from the Fourier transform of the digitized electron micrograph.

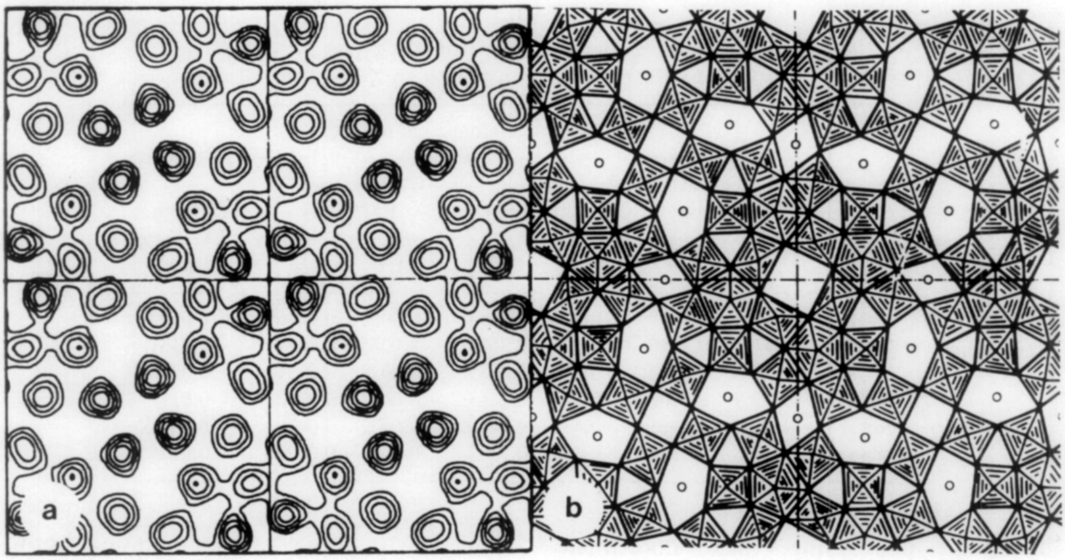

FIG. 3. (a) Contour map of the projected structure of $Na_3Nb_{12}O_{31}F$ after averaging over the 72 unit cells digitized from the electron micrograph and after imposing the fourfold symmetry. The NbO_7 pentagonal bipyramids and NbO_6 octahedra are clearly seen as circular contours of high density. (b) Crystal structure of $Na_3Nb_{12}O_{31}F$ as determined by X-ray diffraction. The NbO_7 bipyramids and NbO_6 octahedra are drawn. The Nb atoms are at the center of each NbO_7 bipyramid and NbO_6 octahedron. The sodium atoms are indicated by small circles. Unit (2 × 2) cells are outlined.

all reflections and printed out in the form of a map. For this crystal, the lowest phase residual was 26°, at a position corresponding to a fourfold symmetry axis. The phase origin was shifted to be on this fourfold symmetry axis and the values of the phases of all reflections were shifted accordingly. The values of the phases of all reflections were given in the fifth column of Table I.

Before calculating the final map, crystal symmetry was applied to the measured data. This was done by averaging the Fourier components in reciprocal space. Noise in the electron micrograph, the deviations of the exact crystal orientation with respect to the electron beam, and electron beam tilt will make amplitudes and phases of the computed Fourier transform deviate from the symmetry-constrained values. Consequently, the values of the phases of all reflection determined in the range -90 to $+90°$ were set to 0°, the rest to 180°. The amplitudes were averaged for all reflections related by fourfold symmetry. The final values of the amplitudes and the phases were illustrated in the sixth and seventh columns of Table I.

The final contour map of the unit cell was obtained by calculating the inverse Fourier transform of the symmetry-averaged centrosymmetric set of structure factors. The map was calculated on a grid of 32 × 32 points along the unit cell edge and contoured at nine levels. Figure 3a shows a contour map of $Na_3Nb_{12}O_{31}F$ with the four highest contour levels. All 24 niobium atoms in the unit cell are clearly seen as peaks of high density in the map and their coordinates are given in Table II. It should be emphasized that this density map was obtained solely by processing of HREM datum and that no previous knowledge of the structure was used in this study. To check the accuracy of the structure determination

TABLE II

FRACTIONAL ATOMIC COORDINATES OF THE Nb ATOMS IN $Na_3Nb_{12}O_{31}F$ DETERMINED BY ELECTRON MICROSCOPY AND X-RAY DIFFRACTION

	Fractional atomic coordinates						
	Electron microscopy		X-ray diffraction		Difference EM/X-ray		Difference EM/X-ray (nm)
Atom	*X/a*	*Y/b*	*X/a*	*Y/b*	*X/a*	*Y/b*	
Nb(1)	0.0654	0.1357	0.0704	0.1393	0.0050	0.0036	0.0108
Nb(2)	0.0731	0.3740	0.0676	0.3689	0.0055	0.0051	0.0131
Nb(3)	0.2478	0.0674	0.2506	0.0785	0.0028	0.0111	0.0200
Nb(4)	0.2509	0.2601	0.2496	0.2663	0.0013	0.0062	0.0111
Nb(5)	0.4299	0.1421	0.4321	0.1450	0.0022	0.0029	0.0064
Nb(6)	0.4478	0.3559	0.4382	0.3588	0.0096	0.0029	0.0175

by image processing, these coordinates were compared with those determined by X-ray diffraction and the average difference in position found by the two methods was 0.013 nm. Figure 3b shows the projected structure model of $Na_3Nb_{12}O_{31}F$ as obtained by X-ray diffraction. It consists of NbO_6 octahedra sharing corners and NbO_7 pentagonal bipyramids sharing edges with five octahedra. The structure can be considered to be a new type of GTB-like structure (*11*).

Conclusion

The contrast of a high-resolution electron microscopy image, taken at Scherzer focus, of a properly oriented crystal thin enough to approximate to a weak-phase object, may be directly interpreted as the local projected structure of the crystal. For a thin and unbent crystal, it is possible to determine the position of metal atoms in the crystal lattice with an accuracy of 0.013 nm, by combining high-resolution electron microscopy and computerized image processing, without using any previous information about the crystal structure.

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