a solid solution or a precipitate of the coexisting phases is formed during high-temperature synthesis in the $A_2O_3-A_2'O_3$ or $A_2O_3-A'O_2$ systems. This is important for a correct interpretation of the measured physical properties of the system under investigation.

Determination of the concentration w of the anionic interstitials from the change in lattice parameter [equation (22)] is important in the interpretation of the physical properties of the solid solution (electrical conductivity, dielectric loss, mechanical properties) and in searching for a correlation between chemical composition and physical properties.

(5) The approximate coordinates of the ions in bixbyite-type compounds and solid solutions can be evaluated from their chemical composition using relations (8), (9), (14)–(22). The agreement between calculated and observed values is reliable (Table 1). The calculated parameters correspond to the most regular bixbyite-type model and they can be used for evaluation of approximate lattice energies.

The results of the detailed crystal-chemical analysis of the bixbyite-type compounds will be used in the investigation of materials based on Y_2O_3.

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The Structure of $NaNb_7O_{18}$ as Deduced from HREM Images and X-ray Powder Diffraction Data

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Abstract

A plausible crystal structure of $NaNb_7O_{18}$ has been deduced from high-resolution electron micrographs and verified by multi-slice calculations of simulated images. X-ray powder diffraction data have been used in an attempt to refine the structure. (JCPDS Diffraction File No. 34-1492). The proposed space group is *Immm*, and the unit-cell dimensions are $a = 14\cdot284\,(3)$, $b = 26\cdot224\,(4)$ and $c = 3\cdot8414\,(6)$ Å, with $V = 1438\cdot9$ Å^3, $Z = 4$, $D_x = 4\cdot437$ g cm^{-3} and $M_r = 961\cdot32$. The structure is related to that of $NaNb_{13}O_{33}$. Na atoms are located in the tunnels characterizing the structure but also at other sites, which provide the same coordination as the perovskite structure. Two types of structure defects, observed in the HREM images, are also presented.

Introduction

In the course of our studies on solid electrolytes we have investigated the system $NaNbO_3-WO_3-Nb_2O_5$ (Hörlin, Marinder & Nygren, 1982). It then became necessary to scrutinize the subsystem $NaNbO_3-Nb_2O_5$ in some detail. This system has been the topic of several studies, and a phase diagram has been given (Appendino, 1973). The existence of a phase found by Appendino, with the approximate composition $Na_2O.4Nb_2O_5$, isotypic with $NaNb_6O_{15}F$ (Andersson, 1965*b*), has been confirmed. Further structural details will be given elsewhere (Marinder, 1983). In this paper, however, we wish to describe another phase in the system $NaNbO_3-Nb_2O_5$, first reported by Shafer & Roy (1959) and confirmed by Appendino (1973), namely $NaNb_7O_{18}$. Some of the

results have been presented at the MICRO 82 conference (Marinder & Sundberg, 1982).

Experimental

Samples were prepared by heating well ground mixtures of $NaNbO_3$ (Pierce Inorganics BV) and Nb_2O_5 (Merck, optipure, purified from oxide fluorides by several hours of heating at 1373 K in air) at 1073 K for 1d and at 1423 K for 2d in sealed platinum tubes and then rapidly cooling to room temperature. X-ray powder patterns were registered in a Guinier–Hägg focusing camera (instrumental profile breadth $0·08° 2\theta$) with monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1·54060$ Å). Potassium chloride ($a = 6·2930$ Å at 298 K) was used as an internal θ standard (Hambling, 1953); $5 \le 2\theta \le 89°$; rotating sample. The positions of the lines and their intensities were evaluated by means of a film scanner system (Johansson, Palm & Werner, 1980). In the refinement of the structure use was made of the programs PIRUM (Werner, 1969), PULVERIX (Yvon, Jeitschko & Parthé, 1977) and SHELX76 (Sheldrick, 1976).

The electron-optical investigation was made with a JEOL JEM 200 CX electron microscope, fitted with an ultra-high-resolution goniometer stage and operated at 200 kV acceleration potential. Electron-microscope samples were prepared by crushing crystals under n-butanol in an agate mortar. Drops of the resultant suspension were collected on net-like carbon films supported by copper grids. Electron diffraction patterns were used for the precise alignment of crystals along a crystallographic axis and for the determination of approximate values of the unit-cell dimensions. Crystal structure images were recorded by the technique described by Iijima (1973) and Allpress & Sanders (1973). The structure model derived from the micrographs was confirmed by calculations of a synthetic electron diffraction pattern and simulated crystal structure images.

A computer program developed by Skarnulis, Liljestrand & Kihlborg (1979) was used for the calculation and plotting of the theoretical electron diffraction pattern. The lattice images were computed from the model by use of the multislice method (Cowley & Moodie, 1957; Goodman & Moodie, 1974) with the aid of a computer program originally written by P. Fejes and J. Skarnulis, and modified by L. Kihlborg.

Results and discussion

The samples from the preparation of $NaNb_7O_{18}$ were white and microcrystalline. Their X-ray powder patterns indicated the presence of small amounts of $NaNb_{13}O_{33}$ and $NaNb_3O_8$ (Andersson, 1967a). This is in accordance with earlier observations that $NaNb_7O_{18}$ is stable only above ~1273 K (Appendino,

1973; Shafer & Roy, 1959). Below that temperature it decomposes to the compounds mentioned above, although it may exist at room temperature as a metastable phase. No crystals suitable for an X-ray single-crystal investigation were found.

From the electron diffraction patterns, approximate dimensions of a unit cell with orthorhombic symmetry were calculated. Starting from these parameters, the X-ray powder diffraction pattern was indexed and the unit-cell axes refined [systematic absences: $h + k + l = 2n + 1$; possible space groups: $I222$ (No. 23), $I2_12_12_1$ (No. 24), $Imm2$ (No. 44), $Immm$ (No. 71); see Abstract and Table 1].*

The diffraction pattern, $(hk0)$ zone in Fig. 1, illustrates that the strongest reflexions form a square network with a subaxis of ~3·8 Å (ReO_3 type), which indicates that the crystal structure of $NaNb_7O_{18}$ has an ReO_3-type substructure. All electron diffraction

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* Table 1 (powder diffraction data) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38966 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
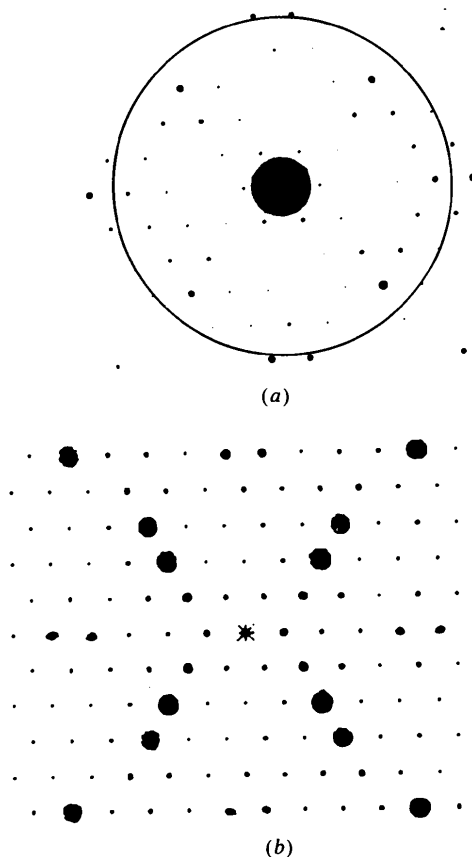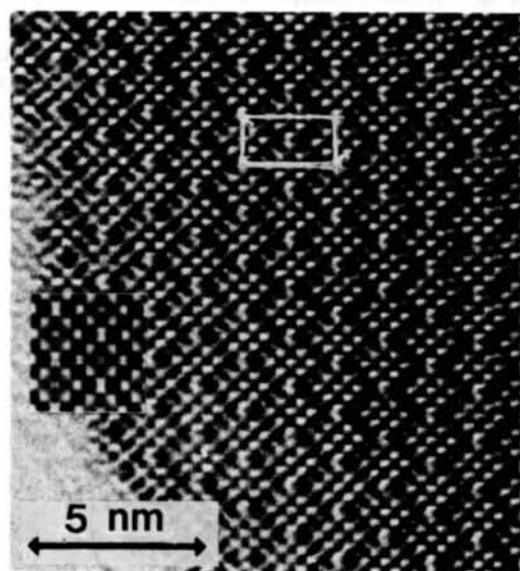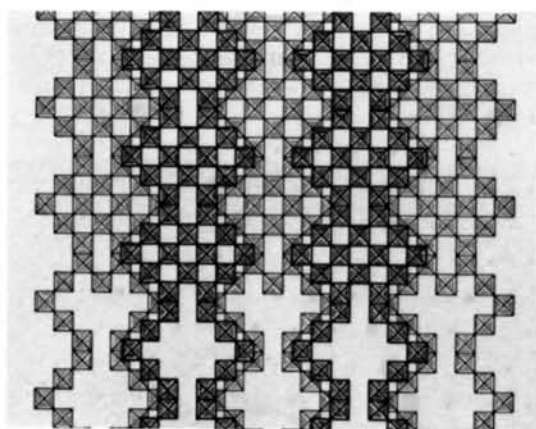

(a)

(b)

Fig. 1. Electron diffraction pattern of $NaNb_7O_{18}$: $(hk0)$ zone. (a) The recorded pattern. The circle inserted shows the objective aperture used. (b) The calculated pattern from the structure model in Fig. 2.

patterns recorded from thin crystal fragments and aligned with the c axis parallel to the electron beam were identical. No streaking of the electron diffraction spots was observed, indicating that the fragments are well ordered.

The crystal structure image shown in Fig. 2 was recorded from a thin crystal flake by including four reciprocal subcell units within the objective aperture, see Fig. 1(a). The image shows that the crystal fragment is very well ordered. A structure model based on this image is also shown in Fig. 2. The black zigzag lines in the micrograph are interpreted as crystallo-

Table 2. *Atomic parameter values as obtained from the structure model of* $NaNb_7O_{18}$

Refined parameter values in italics. Space group $Immm$ (No. 71). Two Na atoms were not considered but are assumed to be situated at the perovskite sites.

	Point position	x	y	z
Na	2(a)	0	0	0
Nb(1)	8(n)	0·10 *0·120 (5)*	0·11 *0·096 (4)*	$\frac{1}{2}$
Nb(2)	8(n)	0·30 *0·305 (6)*	0·22 *0·213 (3)*	$\frac{1}{2}$
Nb(3)	4(f)	0·30 *0·320 (7)*	0	$\frac{1}{2}$
Nb(4)	4(g)	0	0·17 *0·191 (4)*	0
Nb(5)	4(g)	0	0·39 *0·402 (5)*	0
O(1)	8(n)	0·70	0·55	0
O(2)	8(n)	0·90	0·55	0
O(3)	8(n)	0·70	0·67	0
O(4)	8(n)	0·90	0·67	0
O(5)	8(n)	0·90	0·78	0
O(6)	8(n)	0·10	0·11	0
O(7)	8(n)	0·30	0·22	0
O(8)	4(h)	0	0·05	$\frac{1}{2}$
O(9)	4(h)	0	0·17	$\frac{1}{2}$
O(10)	4(h)	0	0·39	$\frac{1}{2}$
O(11)	4(e)	0·30	0	0

5 nm

A B C D E F

A   B   C   D   E   F

Fig. 2. The crystal structure image of a thin flake of NaNb₇O₁₈ is shown at the top. The extensions of a unit cell are outlined. The black, zigzag CS planes are separated by an NbO₃ network. An interpretation of the region A to F is shown below where the CS planes are extended downwards for clarity. A calculated image of the Nb₇O₁₈ model is inserted to the left of the top figure.

graphic shear (CS) planes of the type present in several modifications of Nb_2O_5 and also in $NaNb_{13}O_{33}$ (Andersson, 1965a). The contrast between the black zigzag lines suggests an NbO_3 network of ReO_3 type. The tunnels in the network can easily be distinguished in the micrograph. The unit cell is outlined and corresponds to the stoichiometry Nb_7O_{18}, with $Z = 4$. Two of the Na atoms are assumed to be situated in the tunnels, as is the case in the $NaNb_{13}O_{33}$ structure. The composition of the model structure is then $NaNb_{14}O_{36}$, with $Z = 2$, which means that another two Na atoms must be inserted into the structure to ensure electroneutrality. This poses no problem, however, as several perovskite-type sites are available in the structure. No reduction of the Nb atoms is assumed. Starting from this model approximate atomic parameters were calculated and are shown in Table 2. Using these values, a synthetic electron diffraction pattern, based on the kinematical intensities, was calculated; it is shown in Fig. 1(b). There is fairly good agreement between the calculated and observed electron diffraction pattern.

Synthetic HREM images were calculated, both with and without Na atoms in the large tunnels. The calculations were made at different defocus values and different crystal thicknesses. A synthetic image calculated from the Na-free model of the structure is inserted to the left in the micrograph of Fig. 2. There is good agreement between the observed and calculated images. However, in the micrograph a faint dark contrast dividing the large tunnels in two parts can be distinguished. This contrast is stronger than the

corresponding contrast in the calculated image of the Na-free model of Nb_7O_{18} ($Z = 4$), and rather similar to the contrast obtained from the Na atoms in the calculated image of the $Na_{0.5}Nb_7O_{18}$ structure in Fig. 3. Hence, this feature might be interpreted as being caused by Na atoms in the large tunnels of the structure.

There is, however, a possibility that the Na atoms are too light to be observed and that the observed contrast in the large tunnels may be caused by a very slight misalignment of the crystal in the electron beam. This seems not too likely, however, as identical contrast character has been found in several crystal structure images. The substitution of a heavier atom, e.g. Ag for Na, might clarify the situation. Such work is in progress. It should be noted that the compound $AgNb_7O_{18}$ (Brusset, Gillier-Pandraud & Belle, 1967) is isotypic with $NaNb_7O_{18}$ (Sundberg & Marinder, 1983). We think, however, that the structural similarity with $NaNb_{13}O_{33}$ supports the assumption that Na atoms do reside in the large tunnels.

An attempt was made to refine the structure from X-ray powder diffraction data. As the presence of two extraneous phases made it difficult to apply the technique of profile refinement, it was decided to use simply the integrated intensities as obtained from the film scanner. Thus intensities from 31 well resolved lines on a Guinier photograph were corrected for LPG and multiplicity factors to give the proper structure factors. With space group $Immm$ assumed, these were used in a least-squares refinement of seven positional Nb-atom parameters and one scale factor. Positional parameters of the O atoms and all temperature factors were kept constant. This refinement resulted in a conventional R value of 0·15. The refined values are given in Table 2. The result supports the correctness of the proposed structure.

The structure of $NaNb_7O_{18}$ can thus be described as built up of NbO_6 octahedra having edges and corners in common and arranged in such a way that tunnels of the type found in $NaNb_{13}O_{33}$ are formed (Fig. 4). Blocks of $(4 \times 4 - 2)$ corner-sharing NbO_6 octahedra can be identified. They are linked by edge sharing between component octahedra along the a axis. The slabs of NbO_3 stoichiometry thus formed are regularly arranged at two levels and joined by edge sharing. Na atoms reside in the tunnels and at sites of perovskite-type coordination in the structure. This is essentially the structure anticipated by Andersson (1965c) who, however, assumed $AM_{14}O_{36}$ stoichiometry and monoclinic symmetry. As seen in Fig. 4, $NaNb_{13}O_{33}$ has $(5 \times 3 - 2)$ blocks linked in an analogous manner.

Although most crystal fragments of the new phase were found to be very well ordered, a few defects have been observed. One type of defect is shown in Fig. 5 with its interpretation. The micrograph and the model show that a row (marked by an arrow) of $(4 \times 4 - 2)$ blocks of corner-sharing NbO_6 octahedra has been changed to a row of $(3 \times 4 - 2)$ blocks. The local stoichiometry of this defect corresponds to $ANb_{10}O_{25}$ ($Z = 2$). A structure, $AM_{10}O_{25}$, based on this arrangement was also predicted by Andersson (1965c).

Fig. 6 illustrates a second type of defect found in $NaNb_7O_{18}$. Here, a different contrast in the linkage between the blocks can be observed. In the defect row no large tunnels are visible. An interpretation is also inserted. Here the blocks at the defect are lacking only one octahedron [$(4 \times 4 - 1)$ blocks] and are
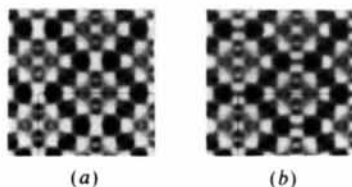

(a)   (b)

Fig. 3. Calculated HREM images: acceleration voltage 200 kV, defocus = −733 Å, objective-aperture radius 0·42 Å^{-1}, $n = 5$ slices (slice thickness 3·84 Å). (a) No Na atoms inserted. (b) Na atoms in the large tunnels.
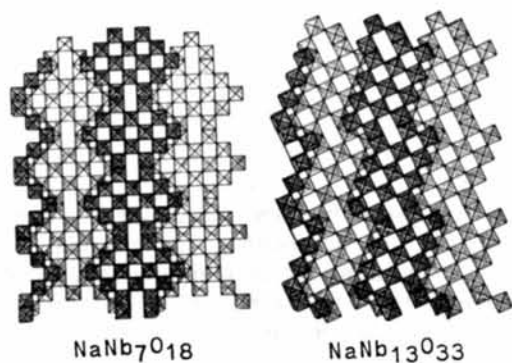

NaNb$_7$O$_{18}$ NaNb$_{13}$O$_{33}$

Fig. 4. The structure models of $NaNb_7O_{18}$ and $NaNb_{13}O_{33}$.
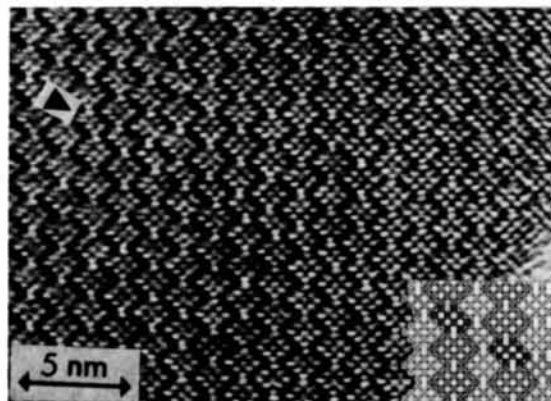

Fig. 5. HREM image of $NaNb_7O_{18}$ showing a defect (marked by an arrow). An interpretation is inserted.

displaced by one octahedron diagonal with respect to each other. This linkage is the same as that occurring in one of the Nb_2O_5 modifications, namely N-Nb_2O_5 (Andersson, 1967b).

In conclusion we note that electron diffraction and crystal structure imaging techniques have been of paramount importance in the deduction of a plausible structure of $NaNb_7O_{18}$. These results will serve as a good starting point for a more accurate structure determination, should X-ray single-crystal diffraction data become available in the future. We also think that continued studies using HREM of $NaNb_7O_{18}$ or similar compounds will reveal further types of structural defects. Such work is now under way.
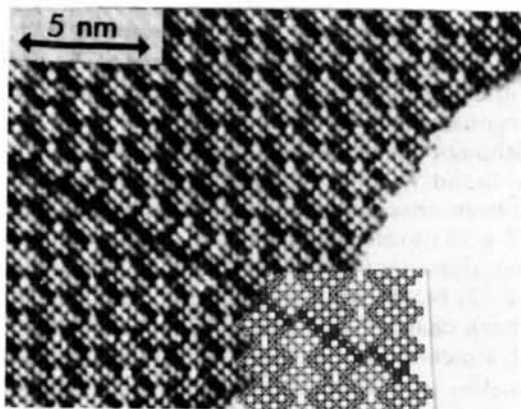
Fig. 6. HREM image of a thin crystal flake illustrating a second type of defect observed in NaNb₇O₁₈. An interpretation is inserted.

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A Crystal Chemical Study of the System CsCl–NaCl–H₂O; Structures of the CsCl Derivative Compounds Cs₁₋ₓ(Na.H₂O)ₓCl, CsNa₂Cl₃.2H₂O, and Cs₂CaCl₄.2H₂O

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Abstract

A restudy of the system CsCl–NaCl–H₂O {previously described by Plyushchev, Tulinova, Kutznetsova, Korovin & Petrova [Zh. Neorg. Khim. (1957). 2, 2212–2220; J. Inorg. Chem. USSR (1957). 2, 357–368]} yielded a new compound, which was found by crystal structure analysis to be $CsNa_2Cl_3.2H_2O$. The crystals ($M_r = 321·27$) are monoclinic, space group $I2/c$, with cell dimensions (from Guinier–Hägg powder refinement) $a = 13·6235 (16)$, $b = 5·8322 (5)$, $c = 10·7053 (12)$ Å, $\beta = 91·26 (1)°$, $V = 850·38 (11)$ Å³ ($= 12 \times 70·9$ Å³), $Z = 4$, $D_x = 2·509$ g cm⁻³, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 50·0$ cm⁻¹, $F(000) = 592$. $R = 0·022$