Ionic Conductivity and the Conductivity-Blocking Defect Structure of NaNb$_{13}$O$_{33}$

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Ionic conduction properties of polycrystalline samples of NaNb$_{13}$O$_{33}$, were investigated between 275 and 450°C by complex-impedance measurements, at frequencies ranging from 5 Hz to 10 MHz. The samples were investigated by X-ray powder and electron diffraction techniques and high-resolution transmission electron microscopy (HRTEM). NaNb$_{13}$O$_{33}$ is shown to be a sodium ion conductor. The sodium ions are most likely conducting in a zigzag manner in planes parallel to [100]. Structural defects blocking the conductivity are identified by a structural image.

Introduction

Compounds with skeletal structures, like NaNb$_{13}$O$_{33}$, have witnessed an increasing interest because of their potential use as material for solid electrolytes (*1*). In the structure of NaNb$_{13}$O$_{33}$ the sodium atoms are lodged in rectangular tunnels with a most likely transport in two dimensions, including jumps into empty perovskite sites of the structure. Many compounds with one-dimensional, two-dimensional, or three-dimensional transport of the conducting ions have been investigated before. For a more extensive review see Ref. (*1*). In order to be able to understand the transport mechanisms of a compound it is important to investigate its local structure. The knowledge of the defect type may make it possible to work out a modified preparation method to get a better performing electrolyte. In some cases the local defects can prohibit transport in certain directions of the structure. This was shown in the case of β''-alumina by high-resolution electron microscopy (HRTEM) (*2*).

Experimental

Samples were prepared by heating a finely ground intimate mixture of NaNbO$_3$, prepared from α-Nb$_2$O$_5$ and Na$_2$CO$_3$ by heating for 2 days at 1100°C, and α-Nb$_2$O$_5$ in the molar ratio 1 : 6 at 1100–1200°C (*3*). The samples were rapidly cooled in air.

X-Ray powder patterns were registered on a Guinier–Hägg focusing camera with monochromatized Cu*Kα*$_1$ radiation. According to the powder pattern the samples were single phases, with data in agreement with Ref. (*4*).

The HRTEM investigation at a structural resolution of 2.5 Å was carried out with a JEOL 200CX, equipped with a top-entry high-resolution ±10° double tilting stage,
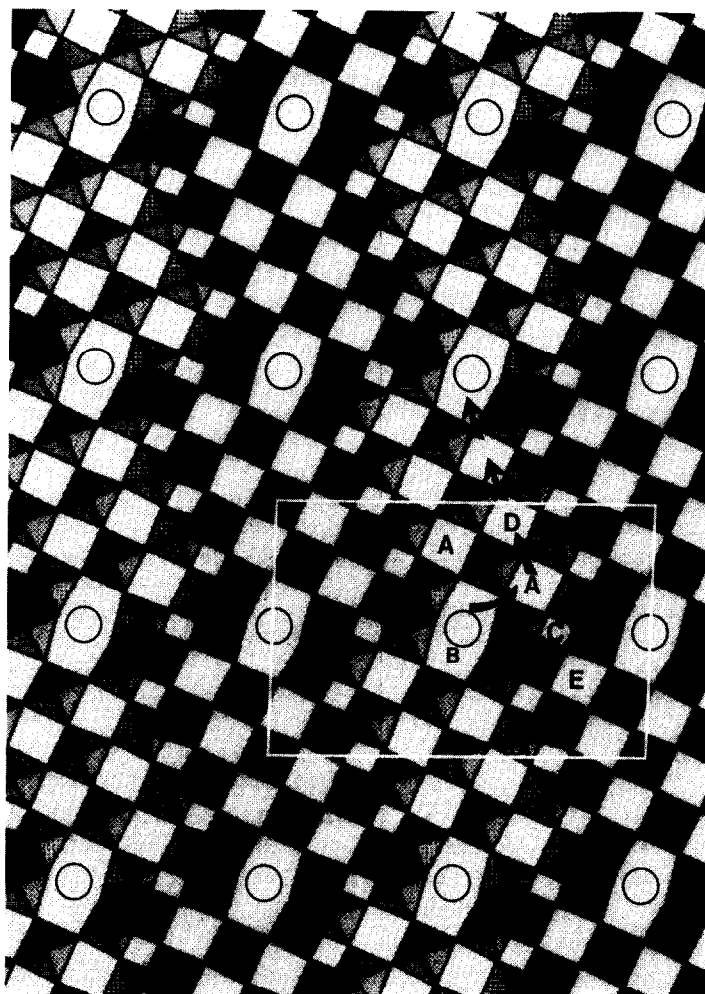
FIG. 1. Polyhedra drawing of NaNb$_{13}$O$_{33}$ projected along [010]. The dark NbO$_6$-octahedra are 1/2*b* up compared to the other octahedra. The sodium ions are marked with large circles. The unit cell is outlined with the *a*-axis horizontal.

operating at 200 kV. Experimental images recorded at Scherzer focus were compared with computer simulated ones in order to verify atomic resolution interpretation of the images.

Compact cylindrical disks, 12.7 mm in diameter and 2 to 4 mm thick with a bulk density of 75–85% of the theoretical density, were prepared by cool-pressing microcrystalline powder at approximately 5 tons/cm². The disks were then sintered at 1150°C for 24 hr. The two opposite sides of the disks were coated with a thin film of platinum conductive paint. The impedance measurements were performed with a Hewlett–Packard 4192A impedance analyzer, with the sample placed in a stream of oxygen-free argon.

Local Structure

The crystal structure of NaNb$_{13}$O$_{33}$ (4) is built up of slightly distorted NbO$_6$ octahedra having corners and edges in common as shown in a [010] projection (Fig. 1). The
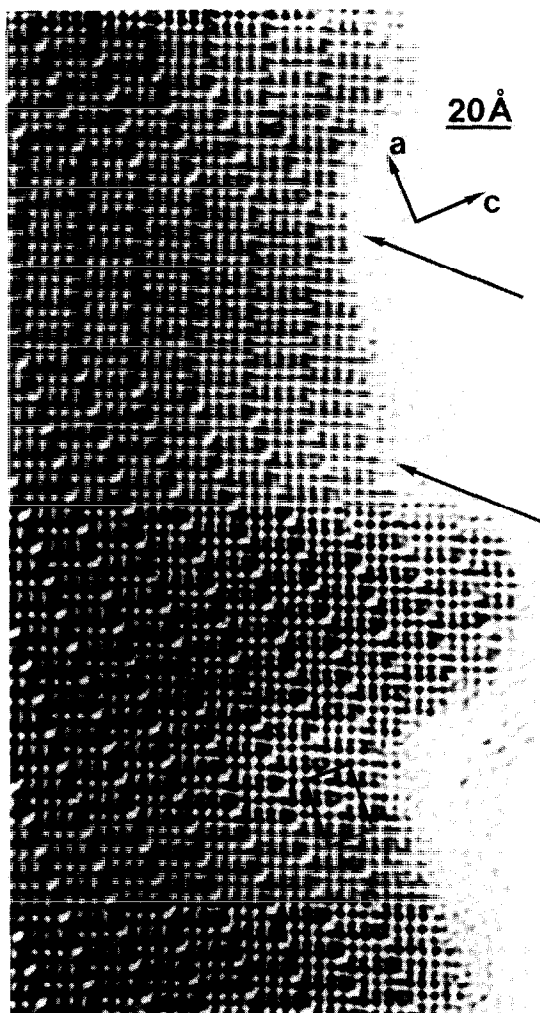
FIG. 2. A high-resolution electron micrograph showing a structural image of $NaNb_{13}O_{33}$ projected along [010]. Every niobium atom in the unit cell inserted can be identified (compare with Fig. 1.). The conductivity-blocking slab of the 5 × 3 blockstructure can be seen between the large arrows.

sodium ions are coordinated to four oxygen atoms at a distance of 2.59 Å. The oxygen atoms form a rectangular plane parallel to the b-axis. The next nearest oxygen atoms form a rectangular plane (Na–O, 2 × 3.39 and 2 × 3.43 Å) perpendicular to the former plane. Similar coordination is known from other sodium titanium oxides (4). The atomic resolution of HRTEM clearly shows the niobium atoms as black spots (compare the unit cell in the polyhedra drawing in Fig. 1 with the marked one in the image).

All crystals studied by means of HRTEM were rich in structural defects. At least three different kinds of defects were identified at atomic resolution. Only the defect possibly affecting the ion transport in the solid will be described here. In most crystals broad slabs of a monoclinic 5 × 3 block structure were found, as shown in the region between arrows in Fig. 2. During the crystal growth process, which has most likely taken place atom-plane by plane perpendicular to [101], there must have been
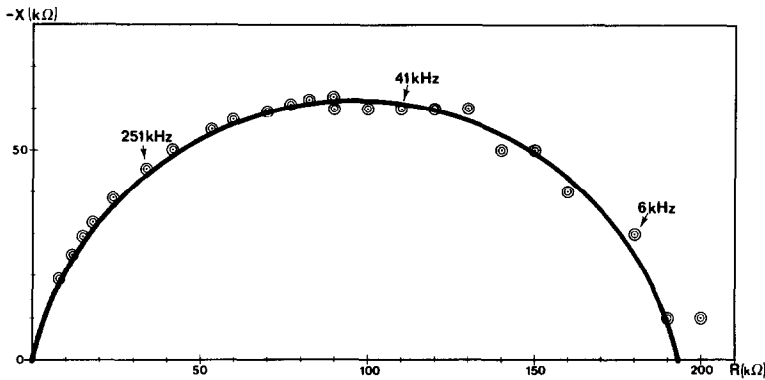
FIG. 3. Complex impedance spectra of $NaNb_{13}O_{33}$ recorded at 300°C with Pt-blocking electrods.

an occasional lack of sodium atoms thus giving rise to a sodium-free 5 × 3 block structure, because sodium ions in the empty perovskite-like positions would give rise to a dark contrast in the electron micrographs (5). This structure obviously joins coherently to the structure of $NaNb_{13}O_{33}$, as can be seen in the image.

Impedance Measurements

Impedance measurements were carried out in the temperature region 275–450°C with a voltage signal of 250 mV and frequencies below 10 MHz. The temperature was regulated by a Eurotherm controller. The resistivity of the disks were found to be reproducible within 5%. A characteristic impedance plot for $NaNb_{13}O_{33}$ is shown in Fig. 3 at 300°C. In all cases a single semicircle (Fig. 3), whose center lies under the real axis, was found. The conductivity was calculated from the disk dimensions and extrapolation of the semicircle to the R axis. Since $\log(\sigma T)$ versus $1/T$ plots are linear over the entire measuring temperature range (Fig. 4), the activation energy for conduction E_a was calculated assuming $\log (\sigma \cdot T) = \log \sigma_0 - E_a/(kT \ln 10)$. E_a and $\log (\sigma_0)$ were determined from least-squares calculations.
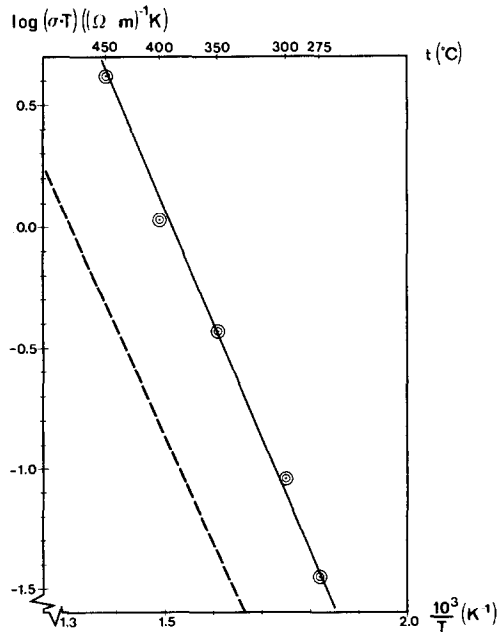
Discussion

$NaNb_{13}O_{33}$ is a moderate sodium ion conductor at low temperatures if it is compared with, for example, MgO-stabilized β-alumina, which has $\sigma_{300°C} = 6.2 \ (\Omega^{-1} \ m^{-1})$ (6). But $NaNb_{13}O_{33}$ is rather good in compari-

FIG. 4. Arrhenius diagram for $NaNb_{13}O_{33}$ compared with the conductivity data of $Na_8Nb_{24}W_{10}O_{94}$, dashed line (6).

son with other sodium ion conductors like Na$_\alpha$Nb$_{16+\alpha}$W$_{18-\alpha}$O$_{94}$ (Fig. 4).

The activation energy, E_a, is reasonably high, indicating the existence of fairly narrow pathways for the conducting ions through the structure. According to the X-ray structure determination all the sodium positions are occupied (4). However the structure contains many empty perovskite-like positions (A in Fig. 1). As a matter of fact a sodium ion in position A will have a mean distance to the 12 nearest atoms of 2.82 Å, which is close to that of the compound of NaNbO$_3$ (2.77 Å) (8). If the sodium ion passes to position A it has to pass a square-like "window" of four oxygen atoms in its corners. The shortest diagonal distance in that square is 3.83 Å. The sodium ion will be able to pass if we assume an opposite thermal vibration of the oxygen atoms of 0.35 Å giving an O–O distance of 4.5 Å. This is a very plausible value according to the thermal factors known (4), at least at the higher temperatures. As soon as one sodium moves from its normal position one ion below can move up to the empty position passing a "window" (B) with a diagonal of 4.3 Å. This window will be passed easier than the former one. A sodium ion in the perovskite position (A) can for the same reasons go farther to another perovskite position D and so on, ending up in a normal sodium site. It is very unlikely that a sodium ion will pass from the perovskite position A through the "window" C to position E because the shortest diagonal of "window" C is only 3.08 Å. Based on structural considerations NaNb$_{13}$O$_{33}$ is therefore most likely conducting sodium ions in a zigzag manner within planes parallel to [100], but the ions cannot jump from plane to plane.

The defect shown in Fig. 2 will act as a blocking defect for the conduction of sodium ions. This illustrates how important it is to determine the local structure of a material before a possible transport mechanism is presented. Materials with a great number of blocking defects like NaNb$_{13}$O$_{33}$ will of course be unsuitable for high-performing materials.

References

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