Short Communication

On the Composition and Ionic Conductivity of $A_{8-x}Nb_{16-x}W_{12+x}O_{80}$ with A = Na, K and Ag

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We have previously studied the composition and ionic conductivity of phases in the system $NaNbO_3/WO_3/Nb_2O_5$[1] with structures related to the tetragonal tungsten bronze (TTB) type. The phase field of the TTB type structure found in this system is shown in Fig. 1. In the course of this work, a new phase with an approximate composition $Na_2Nb_4W_3O_{20}$ was found (marked with an A in Fig. 1). Recently, Marinder and Sundberg reported that this phase had a new type of tunnel structure[2] built up of pentagonal columns which, along the *b* axis of the orthorhombic unit cell, are connected directly to each other via a triangular link, while along the *a* axis the columns are coupled to each other via MO_6 octahedra. Large tunnels with an S-shaped cross section are thereby formed. The Na^+ ions are statistically distributed among two eight-fold sites in the tunnels. The composition was given as $Na_7Nb_{15}W_{12}O_{80}$. The structure analysis revealed an uncertainty in the sodium content of the sample. The number of W and Nb atoms per unit cell found were 12.9(3) and 15.1(3), respectively. Assuming 80 oxygen atoms per cell, this requires 7(3) Na atoms per unit cell. Using the occupancy factors at each Na site as parameters in the least-squares refinement, however, yielded 5.9(8) Na atoms per formula unit. The Na–O distances were also found to be quite long compared to the sum of the Na and O radii, indicating that the Na atoms are too small to fit the tunnels properly. These various observations led us to investigate the homogeneity ranges of the systems

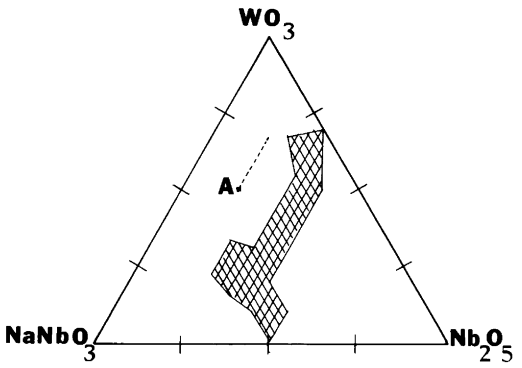

Fig. 1. The shaded area represents the phase field of the TTB type structure found in the systen $NaNbO_3/Nb_2O_5/WO_3$.[1] The compositional range investigated in this study is given by the dotted line. The compositions are expressed in mole percent.

$A_{8-x}Nb_{16-x}W_{12+x}O_{80}$ with A = Na, K and Ag and $0 \leq x \leq 4$ (the dotted line in Fig. 1 shows the range for A = Na). As these studies have been performed within a research project concerning solid electrolyte properties of one-, two- or three-dimensional tunnel structures, ionic conductivity data for these samples are also given.

Experimental

The samples were prepared according to: $(8-x)\ ANbO_3 + 4\ Nb_2O_5 + (12+x)\ WO_3 = A_{8-x}Nb_{16-x}W_{12+x}O_{80}$ with $0 \leq x \leq 4$ and A = Na, K and Ag. All mixtures were ground in an agate

Table 1. Cell parameters for $A_{8-x}Nb_{16-x}W_{12+x}O_{80}$ with A = Na, K and Ag and $0 \leq x \leq 4$. Monophasic samples are marked with an asterisk. The samples with A = K and $x = 3$ and 4 and A = Ag and $x = 2$, 3 and 4 contained only minor amounts of the orthorhombic phase.

A	x	a (Å)	b (Å)	c (Å)	V (Å^3)
Na	0(*)	22.068(9)	17.813(6)	3.928(1)	1544.48
	1(*)	21.972(7)	17.768(3)	3.920(1)	1530.27
	2(*)	21.953(8)	17.762(4)	3.916(1)	1527.14
	3	21.94(1)	17.769(8)	3.914(1)	1525.41
	4	21.942(6)	17.766(3)	3.927(1)	1526.83
K	0(*)	22.005(2)	18.068(2)	3.966(1)	1576.76
	1(*)	22.018(3)	18.047(2)	3.959(1)	1573.08
	2(*)	21.997(4)	18.013(2)	3.952(1)	1565.73
Ag	0(*)	21.942(9)	17.689(6)	3.907(1)	1516.53
	1	21.66(2)	17.72(1)	3.902(2)	1504.56

mortar and fired, first at 973 K for 15 h and then at 1173 K for 72 h, in evacuated silica tubes. The samples were then reground, again placed in evacuated silica tubes and heat-treated at 1173 K for another 50 h. The samples were characterized with Guinier-Hägg focusing X-ray camera, using $CuK\alpha_1$ radiation and Si as internal standard. The intensities and positions of the reflections were evaluated by a scanning system constructed at this Laboratory,[3] and the cell parameters were calculated with the program PIRUM.[4]

The ionic conductivity measurements were performed on sintered pellets within the temperature interval 423–673 K and in the frequency region 1 Hz to 50 M Hz with the use of an impedance spectrometer. The impedance was analyzed using complex impedance plots. The set up and measuring technique are described in Ref. 5. Graphite was used as a material for the blocking electrodes.

Results and conclusions

The lattice parameter variation with x of the orthorhombic unit cell of the Na-containing samples indicates a solid solution range for $0 \leq x \leq 2$ (see Table 1). The X-ray powder photographs of the preparations with $x = 3$ and 4 contained in addition a few unidentified lines. The same homogeneity range was found in the K system. In this case, however, it was found that the additional phase(s) in samples with $x = 3$ and 4 most probably were of TTB or 3-TTB type. The latter structural type is described further in Ref. 6. In the

Table 2. Conductivity data for $A_{8-x}Nb_{16-x}W_{12+x}O_{80}$ samples with A = Na, K and Ag.

A	x	E_a (eV)	$-\log \sigma_o$	$-\log \sigma T$ ($T = 673$ K) (Ω cm)$^{-1}$ K
Na	0	0.81(2)	2.42	3.67
	1	0.84(1)	2.74	3.45
	2	0.72(1)	2.34	2.96
K	0	0.67(1)	1.39	3.68
	1	0.84(2)	2.97	3.31
	2	0.79(1)	2.47	3.37
Ag	0	0.62(1)	2.40	2.19

$Ag_{8-x}Nb_{16-x}W_{12+x}O_{80}$ system, monophasic samples could be prepared only for $x = 0$. All other preparations contained additional phases with TTB or 3-TTB-related structures. The latter samples are presently being investigated using high resolution electron microscopy.

Ionic conductivity measurements were performed on the monophasic samples. Data were collected both during the heating and cooling parts of a complete cycle. A plot of $\log \sigma T$ versus $1/T$ yielded straight lines. The activation energy, E_a, and the preexponential factor, $\log \sigma_o$, were calculated by fitting the data to the equation

$$\log \sigma T = \log \sigma_o - E_a/(2.303 \cdot k \cdot T).$$

The data obtained are given in Table 2, together with $-\log \sigma T$ values at $T = 673$ K. For monophasic samples, the E_a values scatter between 0.84

and 0.62 eV. At 673 K, all samples exhibit moderate conductivity values. $Ag_8Nb_{16}W_{12}O_{80}$ was a better conductor than the corresponding Na and K samples. These were almost equally good conductors. Within the observed homogeneity ranges, a slight increase in ionic conductivity with increasing x value could be traced, but the variation was too small to make any conclusions possible.

The limited solid solution range and the low conductivity values of $A_{8-x}Nb_{16-x}W_{12+x}O_{80}$ with A = Na, K and Ag indicate that the presence of A^+ ions in the S-shaped tunnels is essential for the stability of the structure. Thus in the Na and K systems, at least 75 % of the possible sites for the alkali ions must be occupied in order to prevent the structure from collapsing. In the case of Ag, it seems that no vacancies at all can be tolerated. The latter observation is somewhat puzzling, but can be interpreted to mean that Ag forms TTB and/or 3-TTB-related structures more easily than Na and K within the compositional range studied.

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