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The Existence Range and Related Electrical Transport Properties of β-$Ag_xW_yV_{2-y}O_5$ Bronzes

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The existence range of β-$Ag_xW_yV_{2-y}O_5$ bronzes as a function of x and y has been determined. Cell parameters of the monoclinic unit cell of both β-$Ag_xW_yV_{2-y}O_5$ ($x = y$) and β-$Ag_xV_2O_5$ as a function of x are given. Electrical conductivity measurements were performed on β-$Ag_xW_yV_{2-y}O_5$ ($x = y$) as a function of x and temperature. The diffusion coefficient of silver in the β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$ bronze was measured by means of a galvanostatic pulse technique in the temperature range 200–400°C. A slightly higher diffusion coefficient was observed relative to the pure β-$Ag_{0.35}V_2O_5$ bronze.

Introduction

In the last few years much attention has been paid in the literature to materials potentially suitable as a solid solution electrode in "all-solid-state" galvanic cells. Such a cell can be described as

$$\begin{array}{c|c|l} - & & + \\ M & M^+ - \text{conductor} & M_xTY_n\,. \\ \text{anode} & & \text{cathode} \end{array}$$

The required properties for these materials, symbolized as M_xTY_n, have been described by Steele (*1*). Much work in this field has been done on nonstoichiometric tungsten (M_xWO_3, M = Li, Na) or vanadium ($M_xV_2O_5$, M = Li, Na, Ag) bronzes. In these bronzes the transition metal can be conceived as to have a variable valency. Thus silver vanadium bronzes may formally be described by

$$Ag_xV_2O_5 = Ag_xV^{4+}_xV^{5+}_{2-x}O_5. \qquad (1)$$

In the latter system three single-phase regions exist, the α-, β-, and δ-phases. The homogeneity regions were determined by Casalot and Pouchard (*2*) and are summarized in Table I. In our laboratory a systematic study has been done to describe several electrical and thermodynamic properties of silver vanadium bronzes (*3*, *4*) as a function of the composition parameter x. In the various phases it is possible to replace V^{5+}-ions partly by an amount of W^{6+}-ions within their homogeneity regions. This results in an

TABLE I

HOMOGENEITY RANGES IN THE SYSTEM V_2O_5–$Ag_xV_2O_5$ (*2*)

Phase	Homogeneity ranges in $Ag_xV_2O_5$
α	$0.00 < x < 0.01$
β	$0.29 < x < 0.41$
δ	$0.67 < x < 0.86$

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equivalent quantity of V^{4+}-ions. The compounds obtained in this way can be visualized by

$$Ag_xW_yV_{2-y}O_5 = Ag_xW_y^{6+}V_{x+y}^{4+}V_{2-x-2y}^{5+}O_5 \quad (2)$$

In the present investigation the phase limits are determined for the β-phase as a function of the composition parameters x and y in compounds as given in (*2*). Also unit cell constants for the monoclinic β-phase (space group $C2/m$) are obtained as a function of both x and y. A comparable structural study was done by Darriet *et al.* on Li, Na–W, Mo analogs (*5, 6, 7*). The electrical conductivities were measured as a function of temperature for $Ag_xW_xV_{2-x}O_5$ compounds within the β-region for different values of x.

In addition to diffusion data already obtained for silver in β-$Ag_xV_2O_5$ (*3*), silver diffusion constants were measured at several temperatures for the substituted compound β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$.

Preparation of Materials

Silver vanadium bronzes with partial substitution of W(VI) were prepared according to the reaction schemes

$$x\text{Ag} + y\text{WO}_3 + (1-y)\text{V}_2\text{O}_5 + y/2\text{V}_2\text{O}_4 \xrightarrow{650^\circ\text{C}} \text{Ag}_x\text{W}_y\text{V}_{2-y}\text{O}_5, \quad (3)$$

$$x\beta\text{-AgVO}_3 + y\text{WO}_3 + (1-x-y)\text{V}_2\text{O}_5 + (y+x)/2\text{V}_2\text{O}_4 \xrightarrow{650^\circ\text{C}} \text{Ag}_x\text{W}_y\text{V}_{2-y}\text{O}_5. \quad (4)$$

The used β-silver meta-vanadate in reaction (4) was prepared in accordance with reaction (5)

$$\text{Ag}_2\text{CO}_3 + \text{V}_2\text{O}_5 \xrightarrow[72\text{ hr}]{380^\circ\text{C}} 2\beta\text{-AgVO}_3 + \text{CO}_2\uparrow. \quad (5)$$

The silver carbonate, vanadium pentoxide, vanadium tetroxide, and tungsten(VI)-oxide were all of analytical grade. The preparation of the silver powder, used in reaction (3), was described earlier (*3*). The bronze materials were fired at 650°C in evacuated quartz ampoules for 48 to 72 hr. The batches were reground every 24 hr. A constant cooling rate of <0.5°C min^{-1} of the oven was used in order to obtain homogeneous materials. The color of the bronzes within the β-phase is blue–black like all β-vanadium bronzes.

Experimental

The β-phase limits of $Ag_xW_yV_{2-y}O_5$ compounds as a function of both x and y were determined qualitatively by comparing X-ray patterns obtained by use of a Debye–Scherrer camera. In order to determine the dependence of the monoclinic cell constants of β-$Ag_xV_2O_5$ on x, a Guinier–Lenné camera was used. The cell constants of β-$Ag_xW_yV_{2-y}O_5$ compounds (for $x = y$) for different values of x were calculated from X-ray patterns obtained with a Guinier–de Wolff quadrupole camera.[1] In both cases, high-purity silicon of the U.S. National Bureau of Standards was used as an internal standard.

The electrical conductivity measurements were performed on pressed pellets of polycrystalline material using platinum paint as electrode material. In these experiments an automatic Wayne–Kerr bridge was used at 1592 Hz. A four-probe technique was applied. In preliminary experiments dc and ac measurements at different frequencies were carried out. The diffusion coefficients of silver in β-$Ag_xW_yV_{2-y}O_5$ ($x = y = 0.35$), in conjunction with a silver β-alumina electrolyte, were measured with a galvanostatic pulse technique, using the arrangement described earlier for $Ag_xV_2O_5$ (*3*).

Results

A. β-Phase Limits of $Ag_xW_yV_{2-y}O_5$

The homogeneity region of the β-$Ag_xW_yV_{2-y}O_5$ phase as a function of both x and y is given in Fig. 1. The limits for β-$Ag_xV_2O_5$ ($y = 0$), $x = 0.29$, and $x = 0.41$,

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[1] These measurements were performed by Drs. J. W. Visser, Technische Physische Dienst TNO–TH, Delft, The Netherlands.

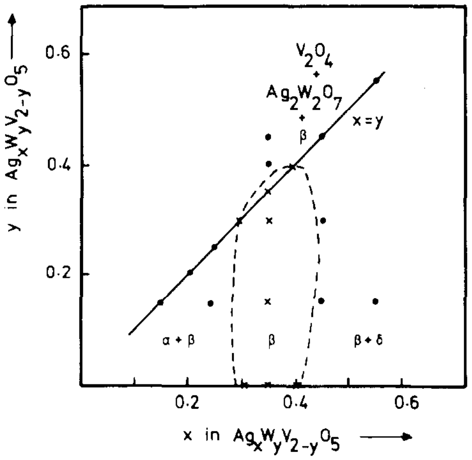

FIG. 1. Existence range of β-$Ag_xW_yV_{2-y}O_5$ as a function of both x and y. ●: In the X-ray patterns several different phases were detected. ×: In the X-ray pattern only β-phase lines were detected.

respectively, were taken from Casalot *et al.* (*2*); compare Table I. The X-ray patterns of the compounds with $x < 0.25$ and $y < 0.25$ showed lines belonging to both an α-phase and a β-phase. For $x > 0.45$ and $y < 0.45$ a β- as well as a δ-phase was observed. The patterns of other compounds outside the given single β-phase region, also showed lines belonging to V_2O_4 and $Ag_2W_2O_7$[2], respectively. The cell constants of the monoclinic β-phase lattice were only determined for $Ag_xW_yV_{2-y}O_5$ compounds on the line $x = y$ (see Fig. 1) for $x = 0.30$, $x = 0.35$, and $x = 0.40$. The calculation of the lattice parameters was done by use of the powder diffraction indexing program ITO, version VI (*8*). The obtained values for the monoclinic lattice constants a, b, c, and β are plotted in Fig. 2, as well as the volume of the unit cell. In the X-ray pattern of the compound with composition parameters $x = y = 0.25$, a number of lines was observed, belonging to an α-phase, with an orthorhombic V_2O_5-like lattice. So the lattice parameters of the compound with $x = y = 0.25$ were calculated using only lines characteristic for a β-phase structure. According to the found phase limits (see Fig. 1), the value of x is in fact about 0.28 ($y = 0.25$). In Fig. 2 the obtained data for β-$Ag_xV_2O_5$ as a function of x are also given. From Fig. 2, it is seen that from all of the four monoclinic cell parameters of the β-$Ag_xV_2O_5$ unit cell only the a-axis is markedly increasing with increasing x. In the case of β-$Ag_xW_xV_{2-x}O_5$ the values of both the a- and c-axes are increasing with increasing x. The b-axis remains almost constant. In Table II some relevant structural data are summarized for β-$Ag_xV_2O_5$ and β-$Ag_xW_xV_{2-x}O_5$.

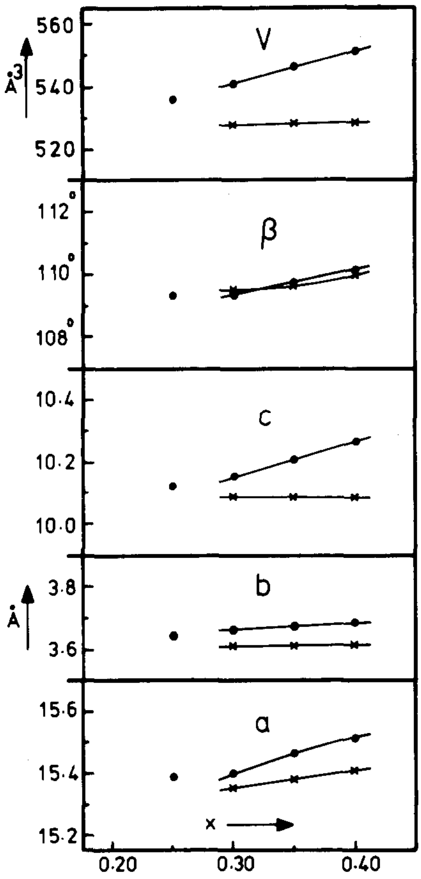

FIG. 2. Cell parameters and volume of the monoclinic unit cell for β-$Ag_xV_2O_5$ and β-$Ag_xW_xV_{2-x}O_5$ ($x = y$). The compound, with $x = y = 0.25$, is according to the β-phase limit in fact $x = 0.28$ and $y = 0.25$, see text. ●, β-$Ag_xW_xV_{2-x}O_5$; ×, β-$Ag_xV_2O_5$.

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[2] $Ag_2W_2O_7$ was prepared by firing Ag_2WO_4 and WO_3 in the correct proportions during 72 hr at 650°C in air.

TABLE II

RELEVANT STRUCTURAL DATA FOR β-$Ag_xV_2O_5$ AND β-$Ag_xW_xV_{2-x}O_5$ AT $x = 0.30$ AND $x = 0.40$[a]

	β-$Ag_xV_2O_5$		β-$Ag_xW_xV_{2-x}O_5$[b]	
	$x = 0.30$	$x = 0.40$	$x = 0.30$	$x = 0.40$
a (Å)	15.359(8)	15.414(3)	15.403(1)	15.517(1)
b (Å)	3.612(2)	3.617(1)	3.666(1)	3.689(1)
c (Å)	10.089(4)	10.086(2)	10.151(1)	10.263(1)
β (°)	109.51(6)	110.00(2)	109.35(1)	110.19(1)
d_x (g cm^{-3})[c]	4.045	4.242	4.680	5.025
V ($Å^3$)	527.6	528.4	540.8	551.4
$d_{I=100}$[d]	3.055	3.052	3.076	3.073

[a] The figures in parentheses indicate the calculated standard deviations.

[b] These data are submitted to the Joint Committee of the Powder Diffraction File.

[c] X-ray density.

[d] Observed d-value of the most intense line in the X-ray pattern.

B. Conductivity Measurements

Electrical conductivity measurements were carried out for β-$Ag_xW_xV_{2-x}O_5$ compounds within the β-phase limits on the line $x = y$. In Fig. 3 the specific conductivity is plotted versus 1000/T (K^{-1}) for these compounds with $x = 0.30$, $x = 0.35$, and $x = 0.40$, respectively. No temperature hysteresis or frequency dependence of the conductivity (from dc to 5000 Hz) was observed. In the range 50–400°C, the electrical conductivity can be described by

$$\log \sigma(T) = \log \sigma_0 - E_{ac}/2.303\, kT, \qquad (6)$$

where E_{ac} denotes an activation energy. The obtained values for E_{ac} as a function of x are tabulated in Table III, together with similar values for β-$Ag_xV_2O_5$ reported earlier (*4*). It can be seen that for β-$Ag_xV_2O_5$ the activation energy decreases with increasing x while the activation energies for the β-$Ag_xW_xV_{2-x}O_5$ compounds show a relative minimum for $x = 0.35$.

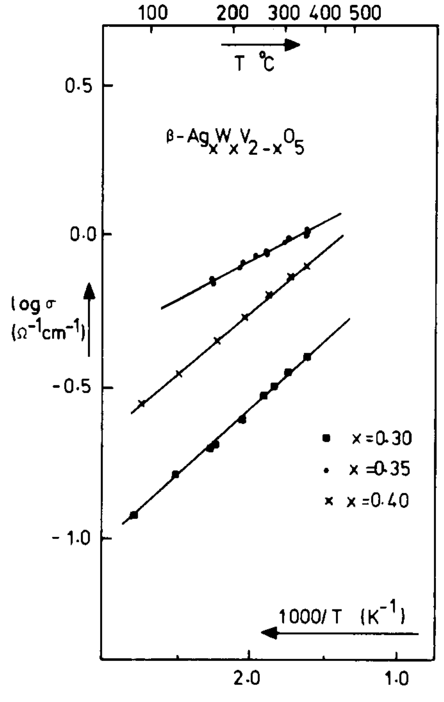

FIG. 3. Specific conductivity vs reciprocal temperature of β-$Ag_xW_xV_{2-x}O_5$ for different values of x.

C. Silver Diffusion in β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$

The silver diffusion coefficient of the compound β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$ was measured as a function of temperature. The results are plotted in Fig. 4. In the same figure the results are given for β-$Ag_{0.35}V_2O_5$, which were already

TABLE III

ACTIVATION ENERGIES OF THE ELECTRICAL CONDUCTIVITY IN β-$Ag_xV_2O_5$ AND β-$Ag_xW_xV_{2-x}O_5$ AS A FUNCTION OF x

	E_{ac} (eV)	
x	β-$Ag_xV_2O_5$	β-$Ag_xW_xV_{2-x}O_5$
0.30	0.113	0.089
0.35	0.091	0.051
0.40	0.079	0.082

TABLE IV

SEVERAL CONSTANTS RELATED TO THE DIFFUSION OF SILVER IN β-$Ag_{0.35}V_2O_5$ AND β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$

Compound	$\log D^{\circ}_{Ag}$	$\log D_{Ag}$ (300°C)	E_{ad} (eV)
β-$Ag_{0.35}V_2O_5$ (*3*)	−7.23	−13.2	0.68
β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$	−7.28	−12.7	0.62

published earlier (*3*). In the range 200–450°C, the diffusion coefficient can be described as

$$\log D_{Ag}(T) = \log D^{\circ}_{Ag} - E_{ad}/2.303\ kT. \quad (7)$$

The calculated results for $\log D^{\circ}_{Ag}$ and E_{ad} for both β-$Ag_{0.35}V_2O_5$ and β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$ are given in Table IV, together with the $\log D_{Ag}$ at a temperature of 300°C. It can be seen that the diffusion of silver is only slightly improved for the substituted compound in comparison with the pure β-$Ag_{0.35}V_2O_5$ bronze.

Discussion

The structure of the monoclinic β-$Ag_xV_2O_5$ phase was at first determined by Wadsley (*9*) and later on by the Hagenmuller group (*10*). The unit cell is given in Fig. 5. In the β-phase vanadium occupies three types of sites, the octahedral sites V_1 and V_2 and a triangular bipyramidal site V_3. Oxygen polyhedra form chains parallel to the *yz* plane: the double octahedral site chains from V_1 and V_2 and the single bipyramidal site chains from V_3. The chains form sheets and have common oxygen ions in the *xz*-plane. It can be seen from Fig. 5 that oxygen polyhedra form sheets parallel to both the *yz*-plane and the *xy*-plane. The octahedral sheets parallel to the *xy*-plane are coupled via the triangular bipyramids. Thus tunnels are formed in the *y*-direction, in which the inserted cations *M* (Li^+, Na^+, and here Ag^+) can reside.

In β-$Ag_xV_2O_5$ at low values of x ($x < 0.33$) the Ag^+-ions occupy randomly the sevenfold coordinated M_1-sites. The distance between two M_1-sites (within the same *xz*-plane, e.g., at $y = \frac{1}{2}$) is about 1.95 Å (*5*). The Ag^+-ion itself has an effective radius of 1.24 Å (7-coordinated) (*11*), so these two M_1-sites cannot be occupied simultaneously (within one *xz*-plane). This implies that a maximal occupation of the sites is reached for $x = 0.33$ in contrast with the expected x-value of 0.67 (obtained from structural considerations). So a zig-zag arrangement of the Ag^+-ions down a

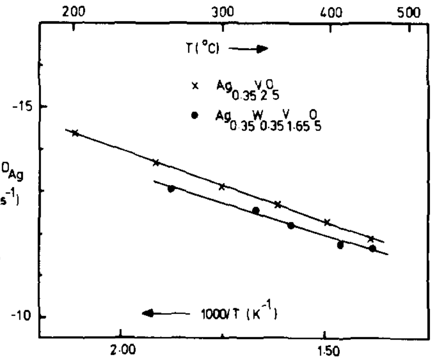

FIG. 4. Silver diffusion constants vs temperature for β-$Ag_{0.35}V_2O_5$ and β-$Ag_{0.35}W_{0.35}V_{1.65}O_5$.

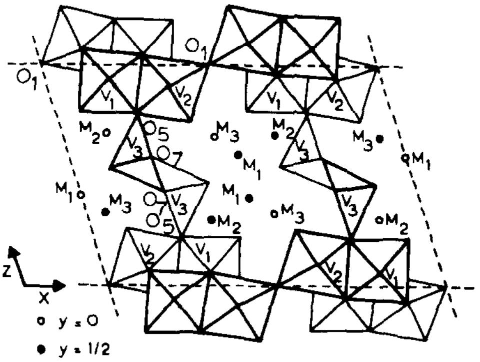

FIG. 5. Possible positions of the inserted cations *M* and vanadium (surrounded by oxygen polyhedra) in the β-$M_xV_2O_5$ structure (from Ref. (*10*)).

tunnel in the y-direction occurs. At $x > 0.33$ alternative sites for the Ag^+-ions must be present: an eight-coordinated site M_2 and a tetrahedral M_3-site (see Fig. 5). It was found, however, by Galy *et al.* (*5*), that excess silver occupies preferentially the M_2-sites.

Darriet *et al.* (*5, 7*) suggested that in β-$Ag_xV_2O_5$ the V^{4+}-ions occupy preferentially the V_1-sites, the excess V^{4+}-ions ($x > 0.33$) the V_3-sites, and the V^{5+}-ions the V_2-sites. From structure refinement calculations it was also concluded that the W^{6+}-ions (in the substituted compounds) occupy preferentially the V_2-sites. The V_3-sites are favored for the excess W^{6+}, at $x > 0.33$, because electrostatic considerations (*5*) prevent the occupation of the V_2-sites up to their theoretical saturation value.

The sheets in the xy-direction can be deformed more easily than the sheets in the yz-direction, because the former are composed of groups of two octahedra, sharing only one corner with the group in the next sheet. So expansion within such a sheet can occur quite easily. The sheets in the yz-direction however are more rigid, because deformation of the bipyramidals must also occur. These facts may explain the increase of the a-axis (see Fig. 2) of the monoclinic unit cell of β-$Ag_xV_2O_5$ when the M-sites are filled on increasing x, while the c-axis remains unchanged. For, this involves a corresponding increase of the V^{4+}-content. The radius of the V^{4+}-ion is somewhat larger than the radius of the V^{5+}-ion (0.59 and 0.54, respectively (*11*)). Both effects mentioned above play a role when tungsten is substituted. However the increase of V^{4+}-content, corresponding to the amount of W^{6+}, now plays a particular role. The radius of the W^{6+}-ion is also greater than the radius of the V^{5+}-ion (0.58 (*11*)). This may explain the larger increase of both a- and c-axis for the substituted β-$Ag_xW_xV_{2-x}O_5$ related to β-$Ag_xV_2O_5$ on increasing x. The same effects were observed in earlier investigations for the Li, Na–Mo, W analogs (*5, 6, 7, 10*).

It can be observed from the data in Table III that the activation energy of the conductivity for the W-substituted specimens shows a minimal value at $x = 0.35$, a phenomenon not mentioned before in literature. Goodenough (*12*) and Bevan and Hagenmuller (*10*) discussed the conduction mechanism for β-$Ag_xV_2O_5$. From various experimental and theoretical considerations it was concluded that the conductivity of β-$Ag_xV_2O_5$ can be explained with a small polaron hopping mechanism. In this model the electrons move in the V_3 subarray. No energy is required for the electron transfer within this V_3 subarray. The relatively low activation energies in this model result from the activated transfer of the electrons from the V^{4+} (d_{zy}-orbital) at V_1-sites via the O_5 sites to the V_3 subarray. This transfer is made possible by the incorporation of the Ag^+-ions on M_1-sites, and at higher x on M_2 and M_3 sites, thereby introducing molecular orbitals (V_3–O_7–V_3) on the V_3 subarray. As the value of x increases, these MO's develop a π^*-band parallel to the tunnels. The activation energy for electron transfer from V_1-sites to this array is decreased at the same time, by the weakening of the individual cation–anion bonding, so that the O_5-ion is more readily displaced towards a V_1-site; hence the activation energy decreases with x, as is also confirmed by our measurements (Table III).

For the observed behavior of the β-$Ag_xW_xV_{2-x}O_5$ phase two opposed effects with increasing value of x should be considered. The first effect is the expected decrease of the activation energy with increasing Ag^+-content as discussed for the β-$Ag_xV_2O_5$ above. The second is the influence of the incorporated W^{6+} on the electrical conduction and the activation energy of this conductivity. Goodenough (*12*) cites unpublished results of Darriet and Casalot on $Na_{0.40}V_{2-y}Mo_yO_5$; these authors observed an increase of the activation energy E_{ac} with increasing Mo^{6+}-content. As already mentioned in our structural discussion the Mo^{6+} is incorporated on V_2-sites, thereby building V^{4+}–O_5–Mo^{6+} deep donors, that contribute electrons to the V_3 subarray at high temperatures. The MO's in the subarray are undisturbed as long as the Na^+-content is kept constant, so that the increasing activation energy with increasing Mo^{6+}-content could be explained by the increased stability of the d_{zy}-orbitals at the V_1-sites through the interaction of the V^{4+}-ions at the V_1-sites with the Mo^{6+} at the V_2-sites.

The same explanation can be used for the β-$Ag_xW_xV_{2-x}O_5$ phase as long as only the effect of the increasing W^{6+}-content is regarded; however, the influence of the Ag^+-content on the activation energy (E_{ac}) is dominant to $x = 0.35$, as can be seen from our experimental data. Above $x = 0.35$ the W^{6+} is incorporated on V_3-sites, thus intruding the V_3 subarray responsible for the conduction. This leads to an extra activation of the conduction process now within the V_3 subarray itself. Together with the increased stability of the d_{zy}-orbitals at the V_1-sites this results in a higher activation energy for the overall conduction.

At the same time the conductivity reaches a lower overall value (see Fig. 3). Above a value of 0.35 for x all the V^{4+}-ions both resulting from the incorporation of W^{6+} and Ag^+ are positioned at the V_3-sites. So the V_3 subarray is disturbed by the incorporated W^{6+} and contains the surplus of charge carriers compared with the 0.35 phase. The conclusion must be that the absolute value of the electron mobility is diminished because the available charge carrier concentration at least equalizes the one at $x = 0.35$. Experimental evidence for this may be expected from Hall-effect and Seebeck measurements. These experiments are in progress now.

The anomaly occurring at $x = 0.33$ is often observed in β-vanadium bronzes (e.g., in thermodynamic functions of $Ag_xV_2O_5$ (*4*) and in the magnetic moment of $Na_xV_2O_5$ and $Ag_xV_2O_5$ (*10*)). According to Bevan and Hagenmuller (*10*) this is possibly due to a 1–1 ordering between the Ag^+-ions and the vacancies within the tunnels, and to the ordering of the W^{6+} in the V_2-sites at a value of $x = 0.33$, which is in agreement with our discussion on the magnitude and the activation energy (E_{ac}) of the electrical conductivity.

The nonspectacular increase of the diffusion constant of silver in β-$Ag_xW_xV_{2-x}O_5$ ($x = 0.35$) with respect to β-$Ag_xV_2O_5$ ($x = 0.35$) as seen from Fig. 4 and Table IV is explained by the expanded tunnel size resulting from tungsten(VI) substitution. In view of the small improvement it can be concluded that at least polycrystalline W-substituted compounds offer no opportunity as a solid solution electrode. This conclusion was made earlier for the pure $Ag_xV_2O_5$-bronzes (*3*).

Acknowledgment

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