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Electrical Properties of Some Silver-Rich Ternary Oxides

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The electrical properties of the silver-rich ternary oxides $AgBO_2$, Ag_3BO_3, $Ag_2Ge_2O_5$, $Ag_6Ge_2O_7$, and $Ag_6Si_2O_7$ were determined by ac impedance, dc polarization measurements with ionically blocking electrodes, and dc transference measurements with electronically blocking ionic conducting electrodes. $AgBO_2$, $Ag_2Ge_2O_5$, and $Ag_6Si_2O_7$ are identified as predominantly ionic conducting compounds with high silver ion conductivities. Ag_3BO_3 and $Ag_6Ge_2O_7$ show predominantly electronic (semiconducting) transport with high partial conductivities of silver ions as the minority charge carriers.

Introduction

Ternary silver(I) oxides with a high ratio of cations to oxygen show unusual structural features with respect to the arrangement of Ag^+ ions, which in spite of their common positive charges tend to aggregate in cluster-like agglomerates (*1*). Even for strongly differing anionic matrices, e.g., in $LiAg_3O_2$ (*2*) and $Ag_6Si_2O_7$ (*3*), these silver partial structures exhibit an impressive topological uniformity: the Ag–Ag distances are of the same order of magnitude as those in metallic silver and the arrangements generally represent sections of the ccp structure of elemental silver. These extensive structural features suggest the existence of weak attractive Ag^+–Ag^+ interactions (*4*). This assumption is supported by the diffuse reflectance spectra in the uv/vis region, which indicate a special electronic state of Ag^+ in this series of compounds: with increasing dimensions of the silver partial structures the absorptions are drastically (by up to 15,000 cm^{-1}) shifted to lower wavenumbers (*5*). In this work we report on the electrical properties which are expected to give further insight into this bonding problem.

Experimental

The crystalline compounds $AgBO_2$, Ag_3BO_3, $Ag_2Ge_2O_5$, $Ag_6Ge_2O_7$, and $Ag_6Si_2O_7$ were prepared from the binary oxides by solid-state reactions. O_2-pressures of about

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200 MPa were applied in order to prevent decomposition of Ag_2O. Detailed preparative data are given in (*6–9*). The substances were handled under exclusion of light as several are markedly light sensitive.[1] The compositions of the samples were ascertained by X-ray powder diffraction work. The compounds were milled and pressed into pellets of 1–3 mm thickness and 10 mm diameter, at a pressure of 50 MPa. Relative pellet densities of 92–96% were thus achieved.

Several techniques were employed for the investigation of the total and partial ionic and electronic conductivities of the samples. The ac impedance was measured using a Wavetek Log Sweep generator (Model 185) to generate sine wave signals with amplitudes between about 5 and 50 mV across the samples and with a frequency range from 1 Hz to 150 kHz. The amplitude and phase shift of the current compared to applied voltage were measured using a PAR two-phase lock-in analyzer (Model 5204) coupled to an X–Y recorder (*10, 11*).

Both ionically blocking and reversible contacts were employed in separate ac impedance measurements. Platinum foil electrodes were pressed against both sides of each pellet as chemically inert and electronic conducting electrodes. Only electronic species may be exchanged across the interface. In addition, silver pellets were used as ionically reversible electrodes for the exchange of both ionic species and electrons.

The partial conductivities of the minority charge carriers were determined by blocking the transport of the majority species and taking readings of the steady-state dc currents through the sample. The ionic current was blocked with the help of a platinum electrode at the positively biased side of the cell. A reversible silver electrode was used at the opposite side in order to fix the composition of the sample at this position (Hebb–Wagner dc polarization technique (*12, 13*)):

$$(-)\ \mathrm{Ag/sample/Pt}\ (+)$$

The partial ionic minority charge carrier conductivity in mixed conducting samples was determined by blocking the electronic transport and allowing the transport of silver ions exclusively. The samples were sandwiched between two α-AgI (above 147°C) solid ionic conductors and elemental silver electrodes:

$$(-)\ \mathrm{Ag}/\alpha\text{-}\mathrm{AgI/Sample}/\alpha\text{-}\mathrm{AgI/Ag}\ (+)$$

Next, dc current–potential curves were taken. Polarization losses of the cell voltage may be eliminated by using two additional AgI/Ag probes along the sample or by briefly turning off the externally applied cell voltage and instantaneously reading the cell potential. The AgI/Ag electrodes which have been applied to block the electronic current act as voltage probes in the latter case. As formation of silver at the sample/electrode interface would cause erroneous results, all such interfaces were microscopically examined. No sign of silver was found.

Results and Discussion

The substances show a total electrical conductivity in the range 10^{-5}–7×10^{-3} Ω^{-1} cm^{-1} at 573 K. Apart from providing estimates of total conductivity, complex impedance measurements allow a preliminary qualitative evaluation of the predominant conduction type. As an example, the complex impedance plane plots of the extremes ($Ag_6Ge_2O_7$, semiconductor; and $AgBO_2$, ionic conductor) are given in Fig. 1. Table I gives a comparison of the energy of the optical absorption edge and the activation enthalpy for electronic conduction. An

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[1] The substances have decomposition temperatures of 320–550°C at ambient pressure.

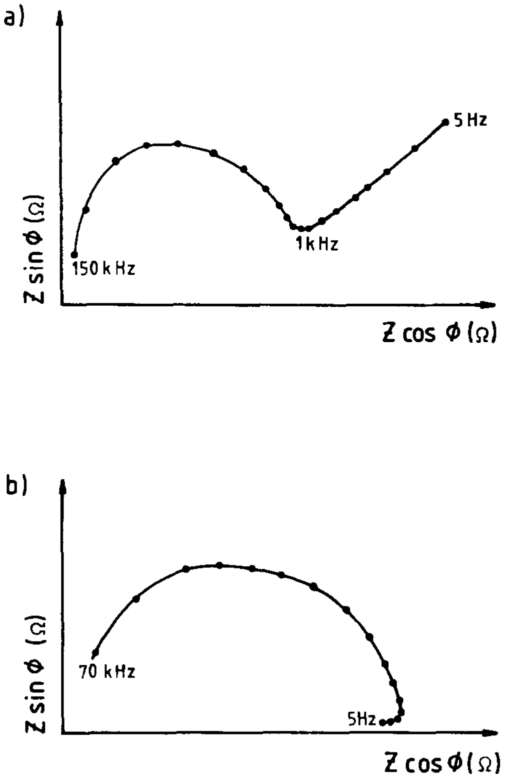

FIG. 1. Complex impedance plane plots of (a) Ag BO_2 (380°C), (b) $Ag_6Ge_2O_7$ (120°C).

at least qualitative relationship seems to exist between these properties.

$AgBO_2$

Alternating current impedance measurements show semicircles in the complex impedance plane with both platinum and silver electrodes. The diameter of the semicircle is taken as the resistance of the sample. Plots of the logarithm of the product of the conductivity and the absolute temperature versus the inverse absolute temperature show an Arrhenius-type behavior for the investigated temperature range from 215 to 470°C (Fig. 2a). The activation enthalpy is 0.64 eV and the preexponential factor is $3.6 \times 10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K which is quite typical for solid ionic conductors and relates to an attempt frequency of the mobile charge carriers of the order of magnitude of the Debye frequency (*14*). The geometrical capacity C_g of the sample is determined from the frequency $n\beta_0$ at the top of the semicircle and the sample resistance R according to $C_g = (2\pi\nu\beta_0 R)^{-1}$. Typical values are in the range from 30 to 90 pF/cm.

A linear voltage–current relation is obtained from dc polarization measurements with the sample sandwiched between two electronically blocking α-AgI pellets (Fig. 2b). The conductivity calculated from the slope of the straight line is in good agreement with the ac conductivity. The polarization is less than one-fifth of the voltage loss corresponding to the sample resistance. The agreement of the ac and electronic blocking dc measurements clearly indicates that $AgBO_2$ is predominantly a silver ion conductor.

The current in the dc polarization experiment with ionically blocking electrodes (sample between Ag and Pt) is only large enough to be measurable above about 410°C. As expected in the case of disordered ionic conductors, Ohm's law is not observed. The electronic transport occurs under the influence of a concentration gra-

TABLE I

COMPARISON OF THE COLOR (ENERGY OF THE OPTICAL ABSORPTION EDGE) AND ACTIVATION ENERGY FOR ELECTRONIC CONDUCTION OF THE COMPOUNDS INVESTIGATED

Compound	Color	Optical absorption edge (eV)	Activation enthalpy for electronic conduction (eV)
$AgBO_2$	Yellow	2.94	~1.1
$Ag_2Ge_2O_5$	Pale yellow	2.89	1.0
Ag_3BO_3	Yellow	2.48	0.81
$Ag_6Si_2O_7$	Red	2.22	0.54
$Ag_{10}Si_4O_{13}$	Red	2.14	—
$Ag_6Ge_2O_7$	Black	—	0.51
$Ag_{10}Ge_4O_{13}$	Black	1.67	—

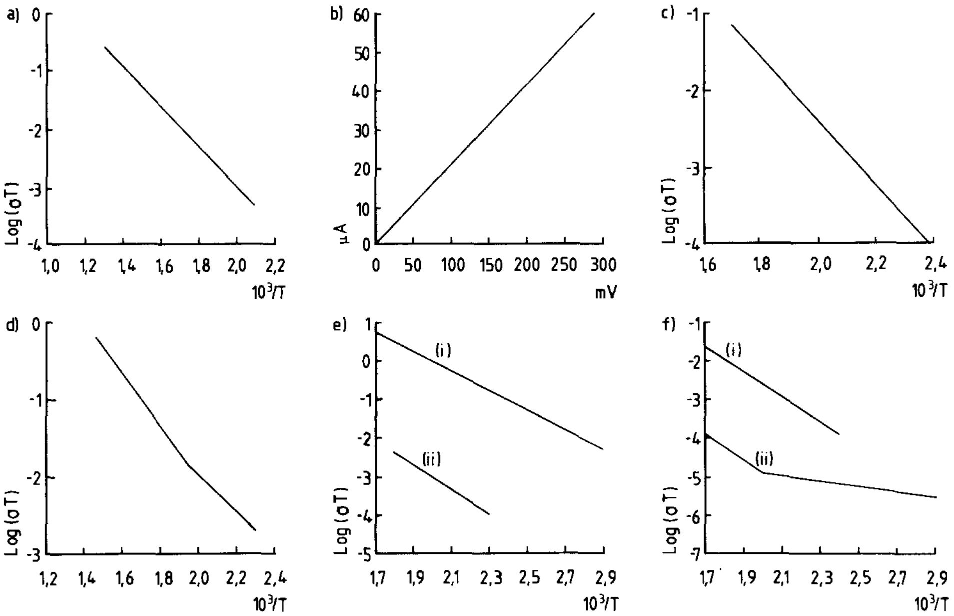

FIG. 2. (a) $AgBO_2$ (ionic conductivity). (b) $AgBO_2$ (V–I relation using electronic blocking electrodes). (c) Ag_3BO_3 (electronic conductivity). (d) $Ag_2Ge_2O_5$ (ionic conductivity). (e) $Ag_6Ge_2O_7$ ((*i*) electronic conductivity, (*ii*) ionic). (f) $Ag_6Si_2O_7$ ((*i*) ionic, (*ii*) electronic conductivity).

dient. A plateau of the current is observed with increasing voltage. This indicates that excess electrons are the prevailing electronic species at silver activities lower than 1. The partial electronic conductivity is at least three orders of magnitude lower than the ionic conductivity.

Ag_3BO_3

The total ac conductivity is identical to the dc conductivity using electronically reversible electrodes in the entire investigated temperature range from 160 to 300°C. Ohm's law is observed in the dc measurements with Pt electrodes. This indicates predominant electronic conduction in Ag_3 BO_3. The transport of the electrons is activated and Arrhenius' law is observed (Fig. 2c). The activation enthalpy is 0.81 eV. The preexponential factor is 5.9×10^5 Ω^{-1} cm^{-1} K which corresponds to common values for the attempt frequency as a result of thermal lattice vibrations of the mobile ions. It may be assumed that the transport of electrons occurs via a hopping process (polaron model).

The silver ions are minority charge carriers in Ag_3BO_3. Long periods of equilibration are required until steady state is reached in dc experiments with electronically blocking ionic conducting AgI/Ag electrodes. Preliminary results indicate an activation enthalpy for the ionic motion of 0.6 eV for the temperature range between 200 and 260°C.

$Ag_2Ge_2O_5$

The results of ac impedance measurements are shown in Fig. 2d. Two regions with distinct straight lines of the logarithm of the conductivity as a function of the inverse temperature are observed: an extrinsic region from 160 to 200°C with an activation enthalpy of the conductivity of 0.46 eV and a preexponential factor of 4.6×10^2 Ω^{-1} cm^{-1} K, and an intrinsic region of conductivity between 200 and 430°C with an activation enthalpy of 0.71 eV and a preexponential factor of $9.3 \times 10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K. $Ag_2Ge_2O_5$ is predominantly ionic conducting. The dc conductivity using electronically blocking ionic conducting AgI/Ag electrodes agrees well with the ac impedance measurements.

Ohm's law is observed in dc polarization experiments using ionically blocking positive Pt and negative Ag electrodes. This is typical for an ionic conductor with a low degree of ionic disorder. The transport of the electronic species occurs under the influence of an electric field. Equilibrium currents are reached quickly after the application of a voltage. The activation enthalpy of the electronic conductivity is 1.0 eV in the temperature range from 250 to 430°C. The preexponential factor is $8.1 \times 10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K.

$Ag_6Ge_2O_7$

$Ag_6Ge_2O_7$ shows predominantly electronic conduction (semiconductor). The diameters of the semicircles in the complex impedance plane yield ac conductivities which agree well with dc polarization results using ionically blocking Pt electrodes. Ohm's law is observed in the polarization measurements. The electronic conductivity is shown in Fig. 2e as a function of temperature. Arrhenius-type behavior is observed for the temperature range from 125 to 305°C. The activation enthalpy is 0.51 eV. A preexponential factor of $1.3 \times 10^5\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K is found.

Linear current–potential curves are observed in the case of the sample being sandwiched between ionic conducting AgI/Ag electrodes. High ionic conductivities are calculated from the slope which are dominated, however, by the transport of electrons. The ionic conductivity shows perfect Arrhenius-type behavior and is also included in Fig. 2c. The activation enthalpy is 0.64 eV in the temperature range from 160 to 280°C. The preexponential factor is $2.5 \times 10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K, which also indicates, in this case of mixed conduction, the typical disorder of solid conductors and attempt frequencies for the ionic motion of the order of magnitude of regular lattice vibrations.

$Ag_6Si_2O_7$

Two semicircles are shown by ac impedance diagrams for $Ag_6Si_2O_7$, one that corresponds to the bulk resistance and a second one which apparently relates to a contribution from the grain boundaries. Electronic blocking ionic transference dc experiments (AgI/Ag electrodes) show the same results as the ac measurements. It is therefore concluded that $Ag_6Si_2O_7$ is predominantly an ionic conductor. The conductivity is shown in Fig. 2f as a function of temperature. The activation enthalpy is 0.64 eV for the temperature range from 150 to 300°C. The preexponential factor is $7.2 \times 10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$ K.

A hybrid between an exponential and linear increase of the current with increased applied voltage is shown by dc Hebb–Wagner polarization experiments with ionically blocking electrodes. This indicates the dominance of holes as electronic minority charge carriers. They move under a mixed influence of a concentration gradient and an electric field. Conductivity values calculated under the assumption of an exponential increase of the current (i.e., the electronic transport is driven by diffusion in a concentration gradient) are several orders of magnitude lower than the values calculated under the approximation of a linear increase of the current (i.e., the electronic transport is driven by an electrical field). The electronic conductivities calculated under the assumption of Ohm's law therefore represent an upper limit of the conductivity of the electronic minority charge carriers. This upper limit of the partial electronic conductivity is also shown in Fig. 2f. The

TABLE II

COMPARISON OF THE RESULTS AND CONCLUSIONS FROM ac IMPEDANCE MEASUREMENTS USING INERT AND REVERSIBLE ELECTRODES AND dc POLARIZATION EXPERIMENTS WITH ELECTRONIC AND IONIC BLOCKING ELECTRODES FOR THE VARIOUS INVESTIGATED SILVER RICH TERNARY OXIDES[a]

Compound	Temperature range, T (°C)	Type of conduction/transference number	Driving force for electrons/mobile electr spec	Ionic disorder	Activation enthalpy, E_A (eV)	Preexponential factor, σT_0 (Ω^{-1} cm^{-1} K)
$AgBO_2$	215–470	Ag^+ $t_e < 0.001$	Diffusion, excess electrons	High	0.64 (Ag^+)	3.6×10^3
Ag_3BO_3	160–300	e^- $t_e \approx 1$	Electric field		0.81 (e^-) 0.60 (Ag^+)	5.9×10^5
$Ag_2Ge_2O_5$	160–200 (extr) 200–430 (intr)	Ag^+ $t_e < 0.01$	Electric field, excess electrons	Low	0.46 (Ag^+, extr) 0.71 (Ag, intr) 1.0 (e^-)	4.6×10^2 (Ag^+, extr) 9.3×10^4 (Ag, intr) 8.1×10^4 (e^-)
$Ag_6Ge_2O_7$	125–305	e^- semiconductor	Electric field		0.51 (e^-) 0.64 (Ag^+)	1.3×10^5 (e^-) 2.5×10^3 (Ag^+)
$Ag_6Si_2O_7$	150–300	Ag^+ $t_e < 0.01$	Diffusion → electric field	Medium	0.64 (Ag^+) (0.54 (e^-))	7.2×10^3 (Ag^+) (5.0 (e^-))

[a] Conclusions on the type of disorder are drawn from the type of driving force for the electronic transport.

activation enthalpy for this upper limit is 0.54 eV for the temperature range from 200 to 305°C. The preexponential factor is 5.0 Ω^{-1} cm^{-1} K. The electronic conductivity of $Ag_6Si_2O_7$ is at least two orders of magnitude lower than the ionic conductivity.

Conclusions

All silver rich ternary oxides ($AgBO_2$, Ag_3BO_3, $Ag_2Ge_2O_5$, $Ag_6Ge_2O_7$, and $Ag_6Si_2O_7$) show high silver ion conductivity in an intermediate temperature range (cf. Table II). In addition, they all show semiconducting properties which may become dominant in some cases (Ag_3BO_3 and $Ag_6Ge_2O_7$). A hybrid transport of electronic minority charge carriers under the influence of a concentration gradient and an electrical field is observed.

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