$AgScO_2$ Revisited: Synthesis, Crystal Structure Refinement and Properties of the Single-phase 3R Polymorph

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Silver scandium oxide $AgScO_2$ has been obtained from Ag_2O and Sc_2O_3 by solid-state reaction at elevated temperature and under high oxygen pressure in stainless-steel autoclaves. $AgScO_2$ was obtained in the 3R Delafossite-type structure, $R\bar{3}m$, with $a = 3.21092(2)$, $c = 18.5398(1)$ Å and $Z = 3$, containing virtually no admixtures of the 2H polytype. The fully ordered structure was solved by high-resolution X-ray powder diffraction data, $R(F^2) = 0.0436$, 30 parameters. $AgScO_2$ decomposes at around 740 °C into Ag and Sc_2O_3 with the release of oxygen. The conductivity of $AgScO_2$ increases gradually with temperature from 5.79×10^{-18} to 7.94×10^{-10} S cm^{-1}, and is ionic in nature, the activation energy for ion conduction being 75 kJ mol^{-1} in the temperature range from 250 to 425 °C.

Key words: Silver, Scandium, Delafossite, High Oxygen Pressure, Crystal Structure

Introduction

Oxides adopting the Delafossite type of structure have experienced a renaissance because of their promising potential for various applications as catalysts [1–5], inorganic phosphors [6, 7] or battery materials [8]. Moreover, those not absorbing visible light have been considered as transparent semiconductors [9–11]. $AgScO_2$, which is expected to be such a transparent oxide, was first mentioned in 1971 [12], but except for the lattice parameters, no further details were given. Recently K. Poeppelmeier *et al.* have described $AgScO_2$ to be a light-grey, air-stable powder. They reported on its optical band gap (3.8 eV) and its electronic conductivity (4×10^{-2} S cm^{-1}) [13], measured using the Powder Solution Composite technique. From the powder diffractogram published in [14] it is obvious that the sample studied was a mixture of the 2H and 3R polymorphs. Here we report on single-phase 3R-$AgScO_2$, synthesized under high oxygen pressure, its structure refinement and electrical properties.

Results and Discussion

$AgScO_2$ is a colorless polycrystalline powder, stable to air and water. According to thermal analyses (DTA/TG/MS) and temperature-dependent XRD data it decomposes at 741 °C into elementary silver, Sc_2O_3 and oxygen. The 3R Delafossite structure type with the general formula $A^+B^{3+}O_2$ has been described earlier in the literature [15]. The value of the lattice parameter *a* directly correlates with the size of the B^{3+} cation. Accordingly, a comparison of $AgScO_2$ with other 3R silver delafossites, *e. g.* $AgAlO_2$ [16] or $AgInO_2$ [17], shows a linear increase of the lattice parameter *a* by increasing the ionic radius of B^{3+}. The Ag–O bond lengths of 2.120(2) Å in $AgScO_2$ are in a good agreement with typical values found for ternary silver oxides [18, 19]. The Sc–O bond lengths of 2.0921(9) Å compare with those in $CuScO_2$ [20]. The experimen-

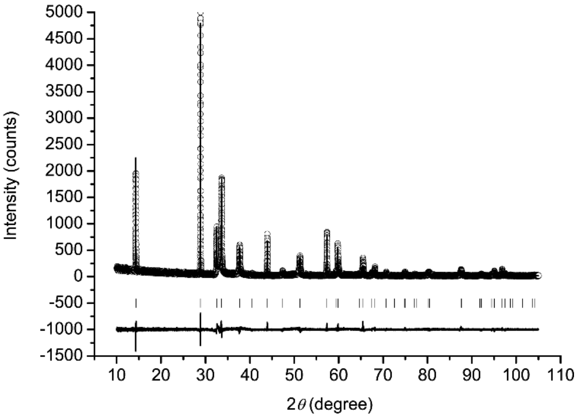

Fig. 1. Observed (circles), calculated (full line) and difference (bottom) powder diffraction Rietveld profiles for $AgScO_2$. The tick marks correspond to the allowed Bragg reflections of $AgScO_2$.

Table 1. Crystal structure data for $AgScO_2$ with estimated standard deviations in parentheses.

Formula	$AgScO_2$
M_r	554.47
Space group	$R\bar{3}m$
a, Å	3.21092(2)
c, Å	18.5398(1)
V, Å^3	165.537(2)
Z	3
D_{calcd}, gcm^{-3}	5.56
Temperature, K	293
Wavelength, Å	1.5406
Starting angle 2 θ, deg	5
Final angle 2 θ, deg	105
Step width 2 θ, deg	0.00853
Scan time, h	20
Refl. measured	38
Param. refined	30
R_{ex}, %	12.55
R_p, %	12.68
R_{wp}, %	16.97
$R(F^2)$, %	4.36
GoF	1.35

Table 2. Final atomic coordinates and equivalent displacement parameters (Å^2 × 10^{-4}) for $AgScO_2$ with estimated standard deviations in parentheses.

Atom	Site	x	y	z	B_{eq}
Ag	3a	0	0	0	0.65(2)
Sc	3b	0	0	1/2	0.65(2)
O	6c	0	0	0.1144(1)	1.3(5)

Table 3. Selected bond lengths (Å) and angles (deg) for $AgScO_2$ with estimated standard deviations in parentheses.

Ag–O	2 ×	2.120(2)	O–Ag–O		180
Sc–O	6 ×	2.0921(9)	O–Sc–O	6 ×	100.24(6)
O–O	3 ×	2.683(3)	O–Sc–O	6 ×	79.76(6)

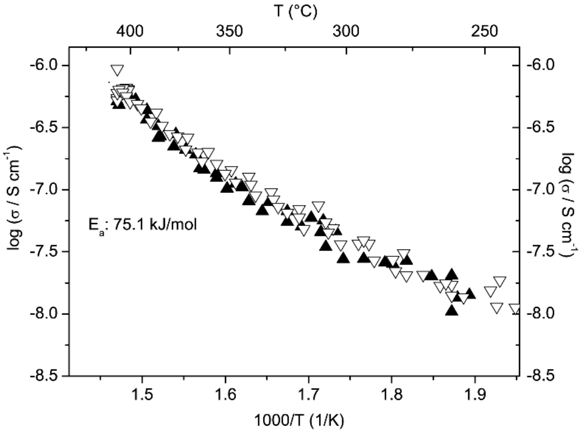

Fig. 2. Temperature dependence of bulk ionic conductivity of $AgScO_2$. Filled symbols represent heating, open symbols cooling.

tal and calculated powder patterns are shown in Fig. 1. Refined structural parameters are given in Table 1. Final atomic coordinates and displacement parameters are listed in Table 2 and selected bond lengths and angles in Table 3.

The temperature dependence of the ionic conductivity of $AgScO_2$ was investigated by impedance spectroscopy. The Arrhenius plot of the temperature-dependent ionic conductivity is displayed in Fig. 2. The corresponding activation energy (E_a) has been derived from the slopes of the conductivity curves to amount to 75 kJ mol^{-1} by using the Arrhenius equation. Between r. t. and 400 °C the conductivity of $AgScO_2$ increases gradually from 5.79×10^{-18} to 7.94×10^{-10} S cm^{-1}. The direct current measurement shows no electron conductivity, proving that the conduction is of ionic nature.

Experimental Section

Synthesis

$AgScO_2$ was prepared by solid-state reaction of Ag_2O (freshly precipitated) and Sc_2O_3 (Alfa Aesar, > 99.9 %) in stainless-steel autoclaves at elevated oxygen pressures and temperatures [21]. Stoichiometric amounts of the components were intimately mixed and placed into gold tubes which were sealed from one side and mechanically closed from the other side. Polycrystalline powder samples of $AgScO_2$ were obtained under an oxygen pressure of 75 MPa within the temperature range from 450 to 500 °C. In a typical experiment, $AgScO_2$ powder was prepared from a mixture of 232 mg Ag_2O (1 mmol) and 138 mg Sc_2O_3 (1 mmol) reacted at 100 MPa and 500 °C for 3 d. The obtained powder was colorless. To improve the crystallinity, 0.2 mL of 1M KOH was added to the mixtures of the components as a mineralizer. The crystalline product was filtered off, washed with deionized water and dried in air.

EDX analyses were carried out on crystals of different samples with a Philips XL 30 TMP, equipped with an energy dispersive micro analyzer Phoenix, EDAX. The Ag/Sc ratio of $AgScO_2$ was found to be close to 1:1.

X-Ray investigations

X-Ray investigations were performed using high-resolution X-ray powder diffraction data (D8, Bruker, Cu$K_{\alpha 1}$ radiation from primary Ge(111) Johannson-type monochromator) at r. t.. The powder diffraction data were collected in the range from 5 to 105° in 2 θ for 20 h. The structure was solved and refined using the program TOPAS [22]. The anisotropic peak width variation was described using the phenomenological model of Stephens [23]. The refined and fitted powder pattern is given in Fig. 1, for the technical details of data acquisition and further crystallographic data see Table 1.

Impedance spectroscopy

Ion-blocking gold electrodes were used to measure ionic conductivity of compact samples (diameter 6 mm, thickness 0.65 mm, pressed with 200 MPa). The samples were placed into a quartz glass cell [24], and the measurements were performed under an argon atmosphere. The temperature-dependent AC impedance spectra were recorded with a Novocontrol Alpha-A 4.2 analyzer in combination with the impedance interface ZG 4 in a 2-wire arrangement in the frequency range $\nu = 1 - 20$ MHz. Measurements and data recording were carried out with the program WINDETA [25]. The bulk conductivities were determined by fitting the non-linear mean square deviation curve of the impedance spectra using the program WINFIT [26].

Thermal analysis

Thermal investigations on $AgScO_2$, simultaneous differential thermal analysis (DTA) and mass spectrum-coupled thermogravimetric analysis (TG/MS), were carried out with an STA 409 (Netzsch GmbH, Selb, Germany) instrument equipped with a quadrupole mass spectrometer (QMS421 Balzers, Hudson, USA). The data were collected between room temperature and 1273 K, using a heating rate of 10 K min^{-1} under a flow of argon.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-422442.

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