PREPARATION AND ELECTRICAL PROPERTIES OF A MONOPHASIC
ZrO_2-Y_2O_3-Bi_2O_3 SOLID ELECTROLYTE

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ABSTRACT

A preparation method is described of monophasic yttria stabilized zirconia doped with Bi_2O_3. This material is prepared from a homogeneous power which, after pressing, is sintered in a Bi_2O_3 atmosphere. The resulting ceramic has a composition of $0.78ZrO_2$-0.206 $YO_{1.5}$-$0.014BiO_{1.5}$. The grain boundaries are enriched with bismuth. A relative density of 95% of the theoretical one is attained at a considerably lower temperature than the bismuth free sample. The electrical conductivities of the monophasic Bi doped and the Bi-free electrolyte material do not differ significantly.

Introduction

Solid electrolytes such as yttria stabilized zirconia exhibit oxygen ion conduction at elevated temperatures. These materials are used for instance in oxygen sensors for the regulation of combustion processes. Electrolyte materials which show a higher ion conductivity are the stabilized bismuth oxides. The (ionic) conductivity at 10 kHz of Bi_2O_3 stabilized with 20 mol% Er_2O_3 is 10 $\Omega^{-1}m^{-1}$ at 800 K [1], while under the same conditions the conductivity of $(ZrO_2)_{0.83}(YO_{1.5})_{0.17}$ (ZY17) is about 0.1 $\Omega^{-1}m^{-1}$ [2]. Another advantage of stabilized Bi_2O_3 compared with stabilized ZrO_2 is the lower sintering temperature (T_S) necessary to achieve a relative density of 95% or more. Stabilized Bi_2O_3 has a sintering temperature of 1120 K [1], while for pure commercial stabilized zirconia T_S is in the range of 1800-2000 K depending on the powder characteristics used in the preparation procedure. The value of T_S for zirconia can be decreased to 1460 K if a sinter-reactive starting powder is used [3,4]. A disadvantage with the use of stabilized Bi_2O_3 is the reducibility and corrosive character at higher temperatures [5,6].
Several investigations have been performed to combine the advantages of stabilized Bi_2O_3 (high conductivity and low sintering temperature) and stabilized ZrO_2 (non-corrosive, low dissociation pressure). This resulted in the ternary system ZrO_2-Y_2O_3-Bi_2O_3 [2,7,8]. A decrease from 1520 K to 1200 K

is found in T_s if Bi_2O_3 is introduced into a sinter-reactive ZY17 powder by dry milling [8]. In most cases however a monoclinic ZrO_2 phase appears when Bi_2O_3 is introduced into $ZrO_2-Y_2O_3$. The presence of a monoclinic phase with low conductivity decreases the mechanical stability and causes deterioration of some of the sensor functions [9,10]. In polyphasic materials the cubic phase tends to reach a composition of $(ZrO_2)_{0.79}(YO_{1.5})_{0.21}$ after completion of the reaction [2,11]. This suggests the occurrence of an invariant point in the ternary phase diagram close to this composition and consequently the impossibility of preparing a monophasic Bi containing material with the optimal Zr/Y ratio for electrical conductivity (ZY17). In this investigation a monophasic ZY21 material doped with Bi_2O_3 was prepared and the electrical conductivity compared with that of pure ZY21 Furthermore these materials were compared with a high purity ZY17 sample, which shows one of the highest conductivities observed for $ZrO_2-Y_2O_3$ materials [3].

Experimental

The high purity ZY17 ceramic powder was prepared by the alkoxide method as reported earlier [4]. This powder was isostatically pressed at 400 MPa and sintered for three hours in a tube furnace as described elsewhere [3].

The Bi_2O_3-free and Bi_2O_3-doped ZY21 powders were prepared by the citrate method as described in [12]. In this way homogeneous precursors could be made of a citrate complex of Zr and Y with or without Bi. These precursors were then thermolysed. The resulting powders were calcined for 24 hours in oxygen at 1070 K, precompacted at 400 MPa and subsequently granulated in order to improve the pressing procedure of the compact. The granulated powders were again pressed. These samples were sintered in different ways; the Bi_2O_3-free ZY21 sample being sintered for three hours in a tube furnace [3].

The Bi_2O_3-doped ZY21 sample, which contains 0.7 at% $BiO_{1.5}$, was first heated to 1070 K with a rate of 100 K/hr, retained for 1 hour at this temperature and cooled down at the same rate. The pellet, with a relative density of 50%, was then cut into disc-shaped samples with a diameter of 15 mm and a thickness of 1.5 mm. These discs were put in a platinum capsule which was placed in the crucible shown in Fig. 1. A powder mixture of yttria stabilized zirconia and Bi_2O_3 (20 wt%) was placed below and around the platinum capsule. This equipment was used to maintain a sufficiently high bismuth oxide vapour pressure over the sample in order to prevent diffusion of Bi out of the sample. In this crucible the samples were heated up to 1420 K at a rate of 100 K/hr, sintered for 3 hours and cooled down at 100 K/hr.

The densities of the samples were measured by an Archimedes technique (in Hg); The ceramic structures of polished and thermally etched samples

FIG. 1

Crucible used for the preparation of the bismuth-doped sample.

were investigated by a JEOL JSM-35CF scanning electron microscope. The grain size was determined according to Mendelsohn [13]. Chemical analysis of the grain boundaries by an energy dispersive X-ray fluorescent method were performed on a JEOL JEM-200 CT scanning transmission electron microscope (STEM)
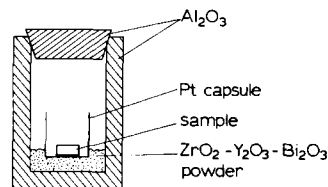
with an EDS unit type (EDAX) mounted on it. The specimen used for STEM was ion-thinned according to [9].X-ray diffraction experiments were performed with a Guinier-Simon camera with $Pb(NO_3)_2$ as the internal standard. A Solartron 1174 frequency response analyser was used for a.c. conductivity measurements on disc-shaped samples with sputtered platinum electrodes. These measurements were performed in the temperature region between 550 and 900 K. Further details concerning the frequency dispersion method are described elsewhere [3].

Results and Discussion

Characterization

In table 1 some material characteristics are given of the samples used for conductivity measurements. The pure ZY17 sample, prepared by the alkoxide method, attained a relative density of 95% at a sintering temperature (T_S) of 1470 K. The resulting grain size was less than 1 μm. A temperature treatment was afterwards given for 3 hours at 1680 K in order to achieve a grain size of 3 μm. The pure ZY21 sample, prepared by the citrate method, attained a density of 95% at 1790 K with a resulting grain size of 9 μm. This confirms that a powder prepared by the alkoxide method is more sinter-reactive than a citrate powder. The alkoxide method however is more time consuming and expensive than the citrate method [4,12].

The bismuth doped ZY21 sample was dense at a sintering temperature of 1420 K (sample ZYB in table 1). This material was sintered in a Bi_2O_3 atmosphere in the crucible shown in Fig. 1. A specimen with the same starting composition (ZY21, with 0.7 at% $BiO_{1.5}$) was sintered in air and attained a relative density of 95% at 1715 K. This air-sintered specimen has a ceramic grain size of 10 μm and contains only 0.1 at% $BiO_{1.5}$ due to volatilization. So it can be concluded that a strong decrease in T_S is found when Bi_2O_3-doped ZY21 is sintered in a Bi_2O_3 atmosphere. A diffusion of bismuth out of the sample and a much smaller decrease in T_S is found when material with the same composition is sintered in air.

TABLE 1

Composition and characteristics of the investigated materials

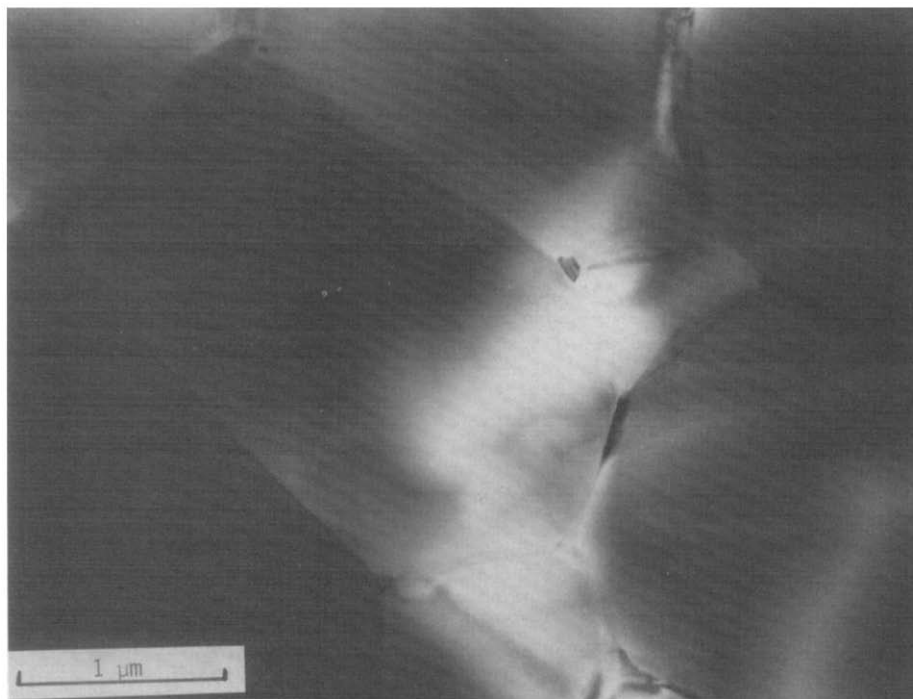| sample code	preparation method	composition (mol%)			T_S (K)	grain size (μm)	cubic lattice constant (10^{-10} m)
		ZrO_2	$YO_{1.5}$	$BiO_{1.5}$			
ZY17	alkoxide	83	17	-	1680	3	5.141
ZY21	citrate	79	21	-	1790	8	5.146
ZYB	citrate	78	20.6	1.4	1420	3	5.152

FIG. 2

TEM picture of ZYB(ZY21 + Bi_2O_3 sintered in Bi_2O_3 atmosphere).

A TEM picture of the ZYB specimen is given in Fig. 2. STEM/EDS analyses were performed on this sample. Zirconium as well as yttrium was detected at all analysed places. The grain boundaries were strongly enriched with Bi. This bismuth-rich film is shown in Fig. 2 as the dark layers between the grains. The thickness of this film is about 10 nm, so that + 1 vol% of the sample is Bi-enriched. This indicates that only 1.4×10^{-2} at% $BiO_{1.5}$ is located in the Bi-rich layer while the major part is situated within the grains. It can therefore be concluded that almost 1.4 at% $BiO_{1.5}$ dissolves in the cubic matrix of the ZYB specimen. The starting citrate powder contains 0.7 at% $BiO_{1.5}$ (see experimental). This indicates that some Bi_2O_3 diffuses into the specimen from the Bi_2O_3 source surrounding the specimen. The bismuth film, present in this sample, and the low melting point of Bi_2O_3 (1100 K) indicate a liquid phase sinter mechanism for the ZYB sample. A liquid Bi_2O_3-rich film is formed around the grains during sintering along which diffusion can take place.

The X-Ray diffraction measurements show that only a cubic phase was detected for all samples. This result and the fact that no Zr-rich phase was found in the ZYB sample indicate that the material is practically a monophasic ZrO_2-Y_2O_3-Bi_2O_3 material. The cubic lattice constants of the samples are given in table 1. The higher value of the lattice constant for ZYB compared with ZY21 is due to the dissolution in the cubic lattice of Bi, which has a higher ionic radius than Zr or Y. Keizer et al. [2] reported a higher dissolution of Bi in ZY21. A few percentages of monoclinic ZrO_2 was sometimes present in these materials.

Electrical Measurements

The frequency dispersion measurements resulted in the complex impedance diagrams as given in Fig. 3. These diagrams are related to grain boundary phenomena [3]. The centres of all semicircles are located only slightly below the Z'-axis. These small depressions indicate uniform bulk and grain boundary properties throughout the sample. The most suitable model to describe ceramic samples with these characteristics is the brick-layer model [3]. In this model it is assumed that the grain-boundary consists of a thin homogeneous layer with a lower specific conductivity than that of the bulk material. This model could be used for pure ZY17 [3]. The ZY21 and ZYB samples almost give the same electrical results, so the brick-layer model may also be used for these materials. This model is electrically represented by the circuit given in Fig. 4. The bulk conductivity (σ_b) as well as the grain boundary conductivity and capacity (σ_{gb} and C_{gb} respectively) per unity of length are determined from the complex impedance diagrams by using the following equations:

$$\sigma_b = 1/R_b = (1/R_1)(L/A)$$
$$\sigma_{gb} = 1/R_{gb} = (1/\{R_2-R_1\})(L/A)$$
$$C_{gb} = (1/\{R_2-R_1\}\omega_m)(L/A)$$

FIG. 3

Complex impedance diagrams in air at 745 K (a) ZY17 ($L/A = 12.73$ m^{-1}) (b) ZY21 ($L/A = 11.46$ m^{-1}) (c) ZYB ($L/A = 8.97$ m^{-1}). The frequency is given in kHz.

where R_1 and R_2 are respectively the high and low frequency intercepts of the semicircles with the real Z'axis. The length/area ratio of the sample is given by L/A, while $\omega_m = 2\pi f_m$ with f_m as the frequency where Z" has a maximal value.

The ZY21 sample has a larger grain size than ZY17 and ZYB (see table 1). Because of this difference in grain size there is a difference in number of grain boundaries per unit length. This effects the value of the grain-boundary conductivity. A correction has been made

FIG. 4

Equivalent electrical circuit representing the diagrams in Fig. 3.

for this effect in order to compare the results i.e. the σ_{gb} values for ZY21 are multiplied by 3/8. In this way all grain boundary conductivities are normalized to specimen with a grain size of 3 μm.

The conductivity as a function of temperature can be described by means of the Arrhenius equation: $\sigma = \sigma_0 \exp(-E_a/RT)$ where σ_0 is the pre-exponential factor, E_a the activation energy for ionic motion, R the gas constant and T
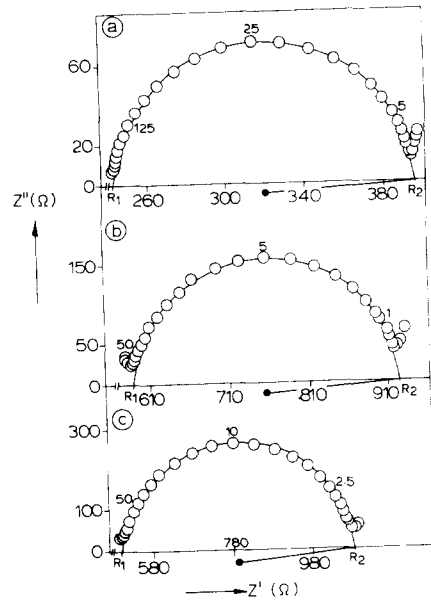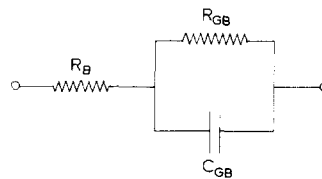
the temperature. In Fig. 5 the con-
ductivity data are shown for bulk
and grain boundaries in the temper-
ature region of 550-900 K. The
values of E_a, log σ_0 and C_{gb} are
given in table 2. It can be seen
from Fig. 5 that, as expected,
ZY17 has the highest conductivity.
Pure and Bi_2O_3-doped ZY21 almost
have the same conductivity. This
implies that introduction of Bi_2O_3
in the ZY21 lattice does not im-
prove the bulk conductivity. At
higher temperatures there is some
improvement of the grain boundary
conductivity due to the introduction
of Bi_2O_3.

The *in*homogeneous Bi-doped Zr-Y
materials, which contain a mono-
clinic phase, show a decrease in
conductivity compared with the Bi-
free samples [2,8]. A ZY17 sample
doped with 2.2 mol% Bi_2O_3, which
contains 20 mol% monoclinic ZrO_2,
shows a large depression of the
grain boundary semicircle in the
complex impedance diagram [8].
This depression is related to *in*-
homogeneous grain boundaries, which
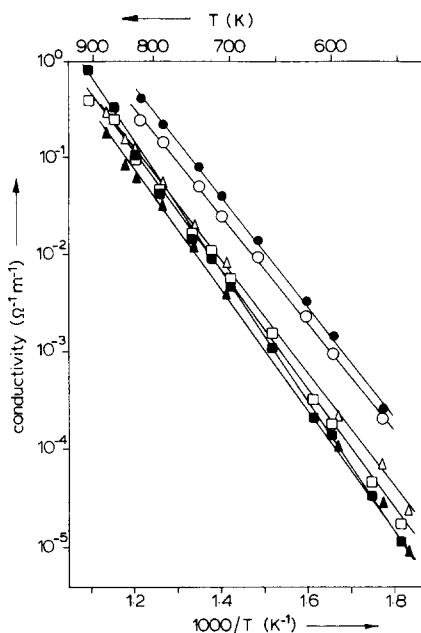are also found by STEM analysis [11].

FIG. 5

Bulk (open points) and grain-bounda-
ry (closed points) conductivities:
ZY17 (O), ZY21* (Δ) and ZYB (□)

TABLE 2

Electrical data

sample code	$E_a(b)$ (kJ mol^{-1})	$\log\sigma_0(b)$ ($\Omega^{-1}m^{-1}$)	$E_a(gb)$ (kJ mol^{-1})	$\log\sigma_0(gb)$ ($\Omega^{-1}m^{-1}$)	C_{gb} (10^{-7} Fm^{-1})
ZY17	105 $\pm$ 2	6.09 $\pm$ 0.18	107 $\pm$ 3	6.47 $\pm$ 0.22	5.80 $\pm$ 0.50
ZY21*	113 $\pm$ 2	6.22 $\pm$ 0.13	118 $\pm$ 3	6.30 $\pm$ 0.20	3.62 $\pm$ 0.45
ZYB	116 $\pm$ 3	6.33 $\pm$ 0.26	127 $\pm$ 3	7.15 $\pm$ 0.21	2.49 $\pm$ 0.23

*) Data for ZY21 are normalized to a grain size of 3 μm . The deviation
is given in the 90% reliability interval.

The conductivity of the Bi_2O_3 rich grain boundary of the ZYB sample,
calculated as a specific conductivity is lower than that of stabilized
Bi_2O_3 [1]. This Bi-film is probably a not-stabilized Bi_2O_3 phase. According

to literature these phases have conductivities which are a factor 1000 lower than the cubic δ-phase [14]. The activation energy for ionic motion in the grain boundary is remarkably high for the ZYB material (see table 2). The activation energy values of the Bi-free samples are in good agreement with the literature data in the temperature region considered [15].

Conclusions

A monophasic bismuthoxide doped yttria stabilized zirconia can be prepared. This material consists of $(ZrO_2)_{0.79}(YO_{1.5})_{0.21}$ (ZY21) doped with 1.4 at% $BiO_{1.5}$ after sintering in a Bi_2O_3 atmosphere. A thin bismuth-rich film is present on the grain boundaries of the ceramic. The major part of the Bi_2O_3 dissolves in the bulk. The bismuth film provides a liquid phase sintering mechanism. A relative density of 95% is obtained at a sintering temperature of 1420 K if this ceramic preparation procedure is used. The conductivity of the Bi-doped ZY21 is slightly higher than that of pure ZY21, but lower than that of the ZrO_2-Y_2O_3 material with the highest conductivity (ZY17).

Acknowledgements

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