

Preparation and Properties of New Oxygen Ion Conductors for Use at Low Temperatures

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Two new systems, $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$ and $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{(CaO)-Bi}_2\text{O}_3$ were investigated. The first system has a homogeneous cubic, fluorite phase between 17.5 and 45.5 mol % Er_2O_3 and can be sintered to densities near 95% at 1200 K. At temperatures between 700 K and 1000 K the highest value of the a.c. oxygen ion conduction in this system is twice as much as the highest value found in the literature. In the second system concentrations of 1-3 mol % Bi_2O_3 act as an excellent sintering aid for $\text{ZrO}_2\text{-Y}_2\text{O}_3$ and $\text{ZrO}_2\text{-CaO}$ samples which can be sintered to densities higher than 95% at temperatures of 1350 K. During this procedure a liquid $\text{ZrO}_2\text{-Bi}_2\text{O}_3$ phase exists from which Bi_2O_3 partly evaporates with increasing sintering time. The oxygen ion conduction is little affected by the Bi_2O_3 -rich second phase. The influence of annealing procedures up to 1570 K on the conduction in the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Bi}_2\text{O}_3$ system is small despite weight losses up to 4%.

1 - INTRODUCTION

Solid state electrolytes are promising materials to use in batteries, fuel cells oxygen probes and sensors, oxygen pumps etc. The stabilized zirconias and bismuth-sesquioxides are good materials for the last three applications because they can have a relatively high conductivity at low temperatures.

The advantages and disadvantages in the properties and the preparation of both types of materials will be briefly discussed now. The stabilized zirconias have a very low dissociation pressure ($< 10^{-30}$ Pa at 1000 K) and can be used up to high temperatures (> 1500 K). The conductivity is relatively low at temperature smaller than 900 K and the sintering temperature of pure stabilized zirconias is larger than 2000 K. Additives such as SiO_2 , Al_2O_3 and TiO_2 are necessary to decrease the sintering temperature^{1,2}. In these cases the densification occurs by a liquid phase mechanism, but the sintering temperature still is at least 1700 K.

After sintering a second phase is present on the grain boundaries. This second phase has isolating properties and sometimes a relatively large electronic component in the conductivity is present. The isolating properties of the second phase decrease the total value of the conductivity of the specimens and an electronic component in the conductivity can have a negative effect on for instance the response time of oxygen sensors⁴.

The stabilized bismuth sesquioxides have a relatively high conductivity at low temperatures (< 900 K) and can be sintered at temperatures near 1300 K to densities larger than 90%⁵. However their oxygen dissociation pressure is 10^{-3} Pa at temperatures of about 1000 K¹³. Above this temperature these materials are corrosive and can react relatively fast with other materials such as platinum.

Our investigation for new oxygen ion conduction materials was centered around two themes:

1 to find a high oxygen ion conductor at low tempera-

tures based on Bi_2O_3 . This resulted in the system $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$ of which the preparation and properties mainly are presented elsewhere⁶ with a summary of some results given in this paper.

2 to combine the advantages of stabilized bismuth sesquioxide (high conductivity and sintering at low temperatures) and stabilized zirconium dioxide (non-corrosive, low dissociation pressure). This resulted in the ternary systems $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{(CaO)-Bi}_2\text{O}_3$ of which preparation and properties are presented and discussed in this paper.

2 - EXPERIMENTAL

For the preparation of the $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$ and $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{(CaO)-Bi}_2\text{O}_3$ samples the raw materials* were thoroughly mixed and pre-fired at 1020-1120 K for $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$ and at 1070-1320 K for $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{(CaO)-Bi}_2\text{O}_3$ during 16 hours (see Table I). The calcinated powders were ground in isopropanol and isostatically pressed at about 400 MPa. For samples with less than 6 at% Bi_2O_3 two firing and grinding procedures were carried out in order to achieve sufficient reactivity.

The samples were sintered in air during 16-70 hours at 1100 K for Bi_2O_3 -rich specimens and at 1350 K for Bi_2O_3 -poor specimens (see Table I). From the sintered samples discs and cylindrical rods were made which were annealed at 1100-1250 K during one hour and cooled down slowly. The total amount of Al_2O_3 and SiO_2 impurities in the samples varied between 0.03 and 0.10 wt% depending on the details of the experimental procedures.

The present phases in the samples were identified

TABLE I - Calcining and sintering temperatures (K) and times (Hrs) of various samples.

SAMPLE *	CALCINATION		SINTERING	
	T(K)	t(hrs)	T(K)	t(hrs)
$\text{Bi}_{1.6}\text{Er}_{0.4}\text{O}_3$	1150	16	1200	70
12, 13	1320	16	1350	70
8, 16	1320	16	1350	70
10, 11	1320	16	1350	16
7, 5	1270	16	1320	16
9, 6	1270	16	1320	16
3, 1	1220	16	1270	70
2	1150	16	1200	70
4, 5	1070	16	1100	16

* Sample compositions can be found in Fig. 2.

* Bi_2O_3 (Merck, very pure, Germany), Y_2O_3 and Er_2O_3 (Serva, 99.9%, Germany), ZrO_2 (Kochlight, England) and CaCO_3 (BDH, England).

Philips PW 1370 X-ray diffractometer with CuK α . The lattice constants were calculated using Pb(NO $_3$) $_2$ as internal standards.

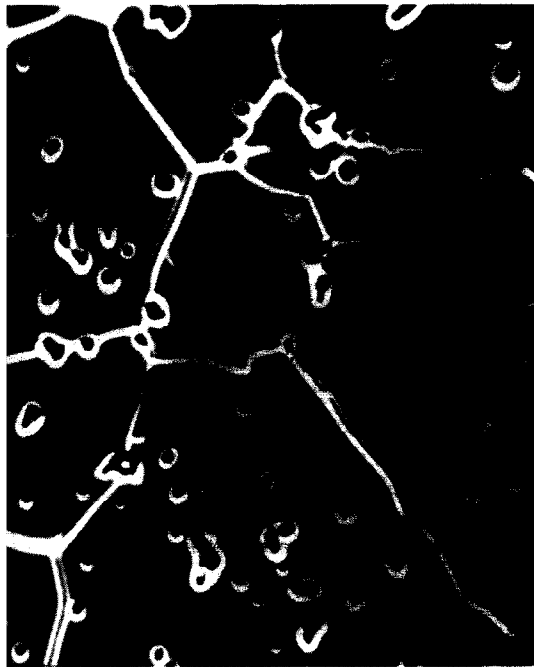
Microstructures were investigated on polished and etched samples with the scanning electron microscope (SEM) type JEOL JSM U3 and an EDAX-unit for chemical analysis of the present phases. The point method was used to determine an average grain size which was corrected according to eq. 10.

Electrical conductivity was measured at 10 kHz by the Wayne-Kerr Universal Bridge B221 of samples with sputtered platinum electrodes of about 10 μ m thickness. The ion transference number was determined by measuring the e.m.f. of an oxygen concentration cell using air at one electrode and pure oxygen at the other electrode. The construction of the concentration cell is given in (Ref. 6).

RESULTS AND DISCUSSION

Microstructures of Bi $_2$ O $_3$ -Er $_2$ O $_3$ specimens

The densities of the specimens after sintering are 80-90% of the theoretical density and the average grain size of all samples is about 30 μ m. The ceramic microstructure of Bi $_2$ O $_3$ -Er $_2$ O $_3$ is shown in Fig. 1.



The ceramic microstructure of 0.8 Bi $_2$ O $_3$ - 0.2 Er $_2$ O $_3$ (magnification 1150x).

From the micrographs one can see that considerable grain growth occurs in this system even at temperatures of 1000°C. The grain boundaries are moving so fast that the grains are isolated within the grains and do not meet at the grain boundaries. This implies that higher sintering temperatures are difficult to obtain unless grain boundary mobility is decreased.

Samples containing 17.5-45.5 mol% Er $_2$ O $_3$ a monoclinic structure was observed with a lattice parameter decreasing from 0.550 nm to 0.540 nm with increasing Er $_2$ O $_3$ -content. Below 17.5 mol% Er $_2$ O $_3$ and above 45.5 mol% Er $_2$ O $_3$ polyphasic regions appear.

Phase relations in the system ZrO $_2$ -Y $_2$ O $_3$ -Bi $_2$ O $_3$

In the investigation of the sintering behaviour of the (CaO)-Bi $_2$ O $_3$ system it was attempted to make

monophasic cubic powder composed of a solid solution of ZrO $_2$, Y $_2$ O $_3$ and Bi $_2$ O $_3$. As a leading idea it was assumed that during sintering a part of the Bi $_2$ O $_3$ separate from the homogeneous phase for instance as a Bi $_2$ O $_3$ -Y $_2$ O $_3$ solid solution.

This second phase acts as a wetting agent of the grain boundaries of the main, cubic phase. The thin, liquid, Bi $_2$ O $_3$ -rich film served as a diffusion path for the sintering procedure and also evaporates slowly. During sintering new Bi $_2$ O $_3$ -rich material on the grain boundaries is delivered from the main phase. After sintering the Bi $_2$ O $_3$ -rich film left on the grain boundaries is not an isolating layer but, on the contrary, has a high oxygen ion conductivity.

To obtain some data about phase relations a small study of possible phases and compositions in the system ZrO $_2$ -Y $_2$ O $_3$ -Bi $_2$ O $_3$ was started. Various samples were prepared with compositions as are shown in Fig. 2. In all these samples only four different phases could be detected; a monoclinic, ZrO $_2$ -rich phase M, a fluorite-type, cubic, ZrO $_2$ -rich phase F, a fluorite-type, cubic, Bi $_2$ O $_3$ -rich phase δ^* and a fluorite type, tetragonal-distorted, Bi $_2$ O $_3$ phase β^* . Samples 3 to 7 and 9* consist of two phases with the F and δ^* structure in sample 3 and the F and β^* structure in the other samples. Sample 6 was suitable to analyze the compositions of both phases with the EDAX-unit of the SEM because the phase separation was large enough to determine the compositions of the distinct phases. The analyzed compositions resulted in the samples 14 and 15.

Several monophasic regions were constructed as shown in Fig. 2 using the literature^{5,7,9} and our own results. The positions of the boundaries are indicated only and are not measured after equilibration at a distinct temperature but after annealing only.

Large kinetic problems can occur at this low temperatures if only little Bi $_2$ O $_3$ is present. For instance the composition 14 in Fig. 2 is a homogeneous second phase in a sample with a composition 6, but it was not possible to realize completely homogeneous samples with a composition 14. Very little is known in the literature about phase relations in this ternary system especially in the ZrO $_2$ -Bi $_2$ O $_3$ region. Therefore in this diagram no phases in the ZrO $_2$ -Bi $_2$ O $_3$ region and no two-phase and three-phase regions are given.

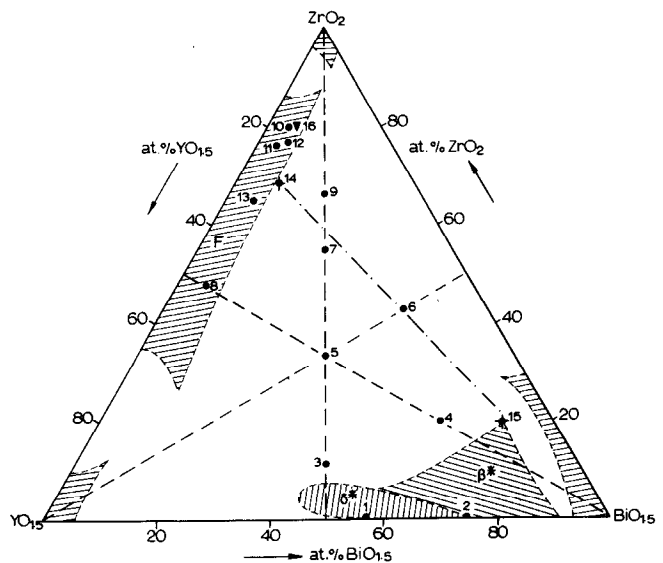


FIGURE 2 - Compositions and phases in the system ZrO $_2$ -Y $_2$ O $_3$ -Bi $_2$ O $_3$ (▼ ZrO $_2$ -CaO-Bi $_2$ O $_3$).

* Sample numbers are equal to composition number in Fig. 2.

3.3 - The sintering behaviour of the system ZrO_2 - Y_2O_3 - (CaO) - Bi_2O_3

Two calcining steps did not result in single phase powders 10 to 14, 16 (Fig. 2) but a main F-phase and a M-phase were present. Powder 8 mainly consists of two F-phases with lattice constants of 0.514 nm and 0.529 nm respectively. After sintering a second phase was still present but the amount of this second phase was diminished and in the ZrO_2 - Y_2O_3 - Bi_2O_3 system the structure was different for calcined and sintered specimens. This is shown in Table 2 together with other results of the sintering procedure. Except sample 8 all the materials sinter to densities near 95% at 1350 K. The ceramic microstructure of samples 12 and 13 are shown in Fig. 3 and Fig. 4 and are typical examples for these types of materials.

TABLE II - Some sintering data and lattice constants of the samples with 5 at% $BiO_{1.5}$.

Sample nr.	Density $\times 10^{-3}$, kg/m ³ (%)	Average grain size (μ m)	Phases ^b
12	5.69 (95%)	3.2	F-phase with $a = 0.5149(3)$ nm + some second phase (<5 wt%)
13	5.72 (97%)	3.8	F-phase with $a = 0.5175(3)$ nm + 10 wt% second phase
8	3.66 (66%)	—	Several F-phases with a varying a between 0.517 and 0.530 nm
16 ^a	5.44 (97%)	≈ 1	F-phase with $a = 0.5153(2)$ nm + 20 wt% M-phase

^a ZrO_2 - CaO - Bi_2O_3 sample; ^b Measured on sintered discs.

The main phase shown in Fig. 3 has an average grain size of 3.2 μ m. The second phase is located on the grain boundaries of the matrix phase. For sample 13 an average grain size of 3.8 μ m is measured however with a relatively large standard deviation. A further analysis suggests that in this case we have a binodal grain size distribution with the smaller grains on the grain boundaries of the larger grains. The large and the small grains have the same composition and are *not* to be identified as two distinct phases. The overall Bi_2O_3 -content, determined after sintering with X-ray fluorescence and EDAX-analyses, appeared to be 3 ± 1 at% in the samples 8, 12, 13 and 16.

The second phase on the grain boundaries as shown in Fig. 3 contains twice as much Bi_2O_3 , an equal amount of ZrO_2 and about half as much Y_2O_3 as the grains themselves, resulting in a composition of about $0.8 ZrO_2 \cdot 0.1 YO_{1.5} \cdot 0.1 BiO_{1.5}$. These figures are limiting values because the second phase regions have a size of 1 μ m or smaller while the X-ray analyses originates from an area with a diameter of 1 to 2 μ m. So the real value of the Bi_2O_3 -content is somewhat larger and the real value of the ZrO_2 and Y_2O_3 contents are somewhat smaller in the second phase. However these analyses give a clear indication that the second phase mainly is a ZrO_2 - Bi_2O_3 solid solution. Although it was more difficult to analyze the second phase in other samples, these second phases are Bi_2O_3 -rich with a relatively high ZrO_2 -content.

The sintering mechanism is somewhat different from that which was proposed before. In our opinion the results suggest, that a mainly monoclinic ZrO_2 - Bi_2O_3 phase becomes liquid at the sintering temperature. This liquid phase is a good wetting agent for the F-phase and during sintering diffusion can take place



FIGURE 3 - The ceramic microstructure of sample 12 (magnification 11,500x).

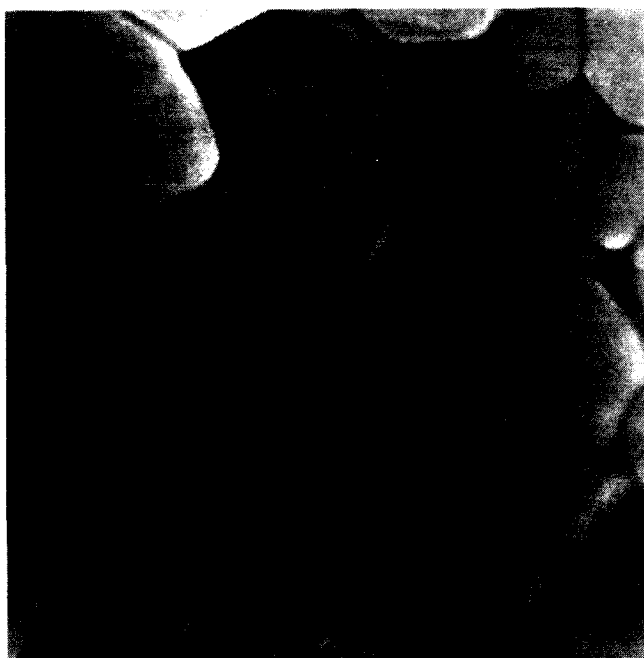
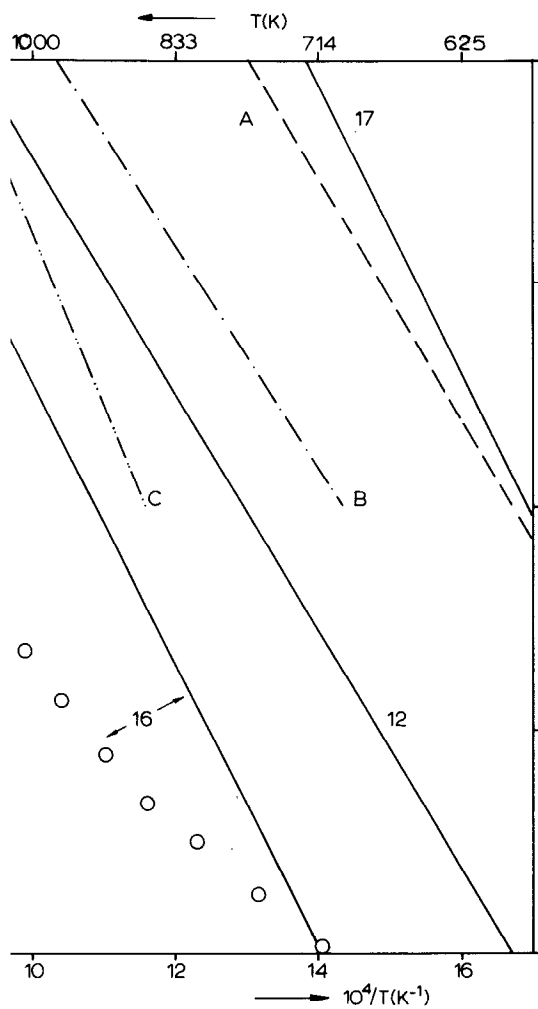


FIGURE 4 - The ceramic microstructure of sample 13 (magnification 11,500 x).

via the liquid phase. In the course of the sintering process a part of the second phase evaporates (Bi_2O_3) and solutes in the F-phase with increasing sintering time.

This proposal is consistent with the observations of weight losses during sintering (1-3 wt %) and a decreasing amount of the second phase during sintering. Perhaps the smaller grains in Fig. 4 are crystallized from the second phase in the initial stages of the sintering process.

The densification of sample 8 is bad probably because the second F-phase does not become liquid at the sintering temperature.



The a.c. conductivity as a function of temperature samples (sample numbers see Fig. 2 and Table 2; annealed at 1750 K).

uctivity in the systems Bi₂O₃-Er₂O₃ and Y₂O₃-(CaO)-Bi₂O₃

and Fig. 6 the a.c. conductivity as a function of temperature is shown. The numbers of the samples and the composition as shown in Fig. 2 and Table 2. Some data concerning the conductivity as a function of the values is given. If the conductivity in the Bi₂O₃-Er₂O₃ system is compared with the highest values given in the literature then it appears the Bi₂O₃-Er₂O₃ system has the highest oxygen ion conductivity known. Furthermore the conductivity in the ZrO₂ samples contains about half a decade lower (Fig. 5) than the highest values given in the literature for the ZrO₂-CaO systems at the maximum in the conductivity-composition curves at the same temperature. The reason for this difference is firstly that the Bi₂O₃ ratio of our samples deviates from that of the samples with a optimal conductivity. Secondly it is the composition which has the highest value of conductivity in this ternary system. It was not the purpose of this investigation to study that problem. The lowering of the conduction is possible because monoclinic second phase possess insulating properties. One sample (11, see Fig. 2) has no second phase after sintering and indeed has the highest ionic conductivity. An electronic component in the total conductivity is small because all ion transference numbers in Table 2, are within the standard deviation

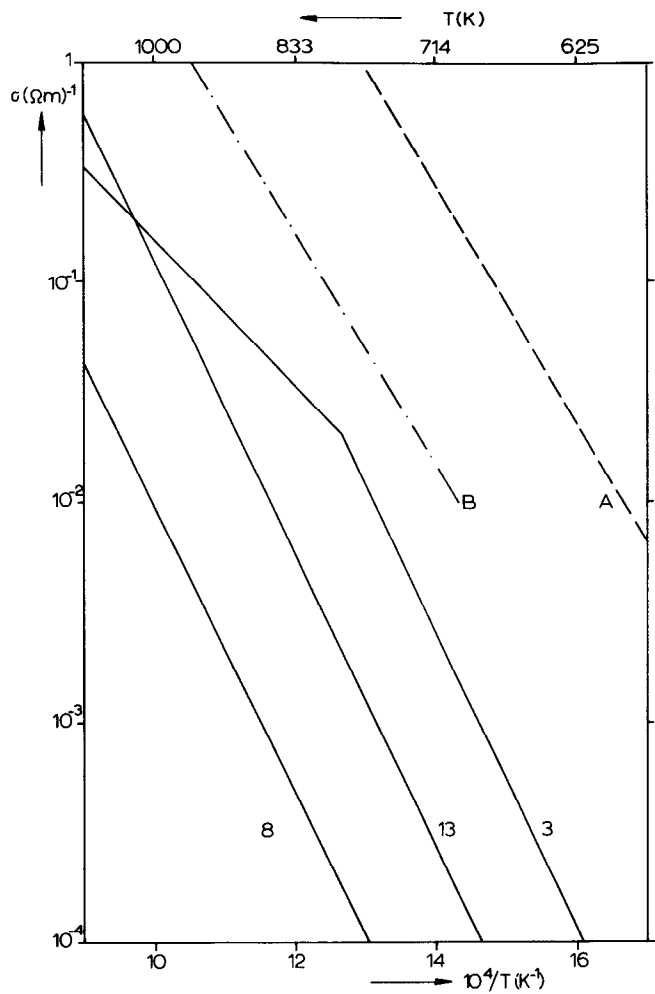


FIGURE 6 - The a.c. conductivity as a function of temperature for various samples (sample numbers see Fig. 2 and Table 2).

TABLE III - Activation energy E, sigma₀ values and transference numbers t_i of the conductivity of various samples.

Sample nr. ^a	E(kJ/mol)	sigma ₀ x 10 ⁻⁵ (Ohm) ⁻¹	Transference number t _i
3	127	—	—
8	123	0.3	—
12	102	1.0	0.97 (800-1000 K)
13	128	6	0.97 (800-1000 K)
16	120	0.6	0.99 (800-1000 K)
17	115	1300	0.98 (770-1070 K)
A	106	190	0.98 (750-1050 K)
B	92	1.3	1.00
C	136	11	1.00

^a 17: 0.80 Bi₂O₃-0.2 Er₂O₃
 A: 0.75 Bi₂O₃-0.25 Y₂O₃
 B: 0.91 ZrO₂-0.09 Y₂O₃
 C: 0.25 ZrO₂-0.15 CaO.

for this method (3-5%) equal to one. Annealing procedures were carried out at 1220 K and 1570 K during 100-500 hours. The effect of this procedure on the value of the conductivity in the ZrO₂-Y₂O₃-Bi₂O₃ system is smaller than 10%, relative although weight losses up to 4% (2 at % BiO_{1.5}) occur at the

highest temperature. The effect of the value of the conductivity in the ZrO_2 -CaO- Bi_2O_3 system was larger. At 1220 K the conduction decreases 20% after 300 hours annealing but there were no weight losses. At 1570 K an annealing of 100 hours causes a weight loss of 2.3% and a collapse in the conductivity especially at higher temperatures (see Fig. 5, curve 16). It is not clear which mechanism causes this strong decrease in conductivity in this case.

4 - CONCLUSIONS

Samples in the system Bi_2O_3 - Er_2O_3 and ZrO_2 - Y_2O_3 (CaO)- Bi_2O_3 were prepared at temperatures of 1100-1350 K with densities near 95% or higher and grains of about 30 μm in the Bi_2O_3 - Er_2O_3 system and of 1-4 μm in the ZrO_2 - Y_2O_3 (CaO)- Bi_2O_3 system. In the samples with nominal 5 at% $BiO_{1.5}$ of this last system a second phase with a monoclinic or a cubic structure appeared after pre-heating the powders at 1320 K. After sintering at 1350 K the second phase mainly consists of a ZrO_2 - Bi_2O_3 solid solution which forms a liquid at the sintering temperature. It acts as a wetting agent and therefore as a reactive sinter aid but during sintering it partly evaporates.

The values of the a.c. oxygen ion conduction in Bi_2O_3 - Er_2O_3 (1 Ωm at 720 K) are two times larger than in Bi_2O_3 - Y_2O_3 (5), which is one of the best oxygen ion conductors known in the literature. In the ternary systems the oxygen ion conduction is somewhat smaller than the highest values found in the literature for the corresponding systems but no attempt was made to find the optimal compositions for the conduction in this system. Furthermore annealing procedures at 1220 K and 1570 K did not alter the conduction in the ZrO_2 - Y_2O_3 system. In the ZrO_2 -CaO system an annealing temperature of 1570 K decreases the conduction at higher temperatures but a mechanism for this effect is not known.

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