

**BISMUTH OXIDE BASED CERAMICS WITH IMPROVED ELECTRICAL AND
MECHANICAL PROPERTIES**

PART II. STRUCTURAL AND MECHANICAL PROPERTIES

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ABSTRACT

Coprecipitation as a method of preparation for bismuth oxides based ceramics yields relatively strong and machineable materials in comparison with the solid state reaction. Compositions within the system $(1-x)\text{Bi}_2\text{O}_3-x\text{Er}_2\text{O}_3$ containing up to twenty five mole percent of erbium oxide show a slow transition on heating at 900 K from a cubic to a hexagonal (rhombohedral) phase. The resulting hexagonal phase is stable up to 1000 K where it transforms back to the cubic phase. Long term heating at 775 K causes formation of traces of α - bismuth oxide in these samples, but the material itself remains cubic. Compositions containing thirty mole percent of erbium oxide do not show any such changes and hence are suitable for application purposes.

MATERIALS INDEX : Bismuth, Erbium, Oxides.

INTRODUCTION

Oxygen ion conducting solid electrolytes find extensive

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use in devices such as oxygen pumps and - sensors. For these type of applications the stabilized cubic bismuth oxides have significant advantages over the conventional stabilized zirconias, due to their ability to operate at lower temperatures with better efficiency (1-3). This behaviour is based on the high temperature ionic conducting δ - bismuth oxide, which can be stabilized to lower temperatures by doping with various rare earth oxides (4-6). Among these, the solid solutions of bismuth erbium oxides have the highest ionic conductivities reported (2,7). In the first part of this report (8), some aspects of the preparation of bismuth erbium oxides were highlighted. Through preparation by a coprecipitation method it was possible to form dense and machineable ceramics. To understand the durability of such compositions under practical conditions however, a study of compositional, structural, morphological and mechanical properties is crucial. The results of such measurements are reported here.

EXPERIMENTAL

The details of preparation have been reported in part I (8). A description of the sample code is given in Table 1. Differential Thermal Analysis (DTA) of the samples was carried out on a Du Pont 990 model Thermal Analyzer, using heating/cooling rates of 5 K/min. The mechanical strength (σ_f) was measured on samples with dimensions of 1 * 3 * 15 mm. A three-point bending test was used (9,10), with a span of 12 mm and at a cross head speed of 5 $\mu\text{m s}^{-1}$. The samples were cut from sintered discs with a high speed diamond cutting wheel. Before strength measurements the samples were annealed at 1025 K for 4 hours, using heating/cooling rates of 2 K/min.

TABLE 1
Description of sample code

Sample code	Description
BEXX	XX corresponds to the mole percent of erbium oxide.
P	Prepared by coprecipitation method.
S	Prepared by solid state reaction of oxides at 1125 K.
A	Cubic samples annealed at 775 K for 500 hours.
B	Cubic samples annealed at 900 K for 500 hours.

RESULTS AND DISCUSSION

Samples prepared by coprecipitation as well as by solid state reaction have been used for various studies. Both methods yield monophasic and homogeneous materials.

i. Thermal studies

DTA curves of samples after various heat treatments are

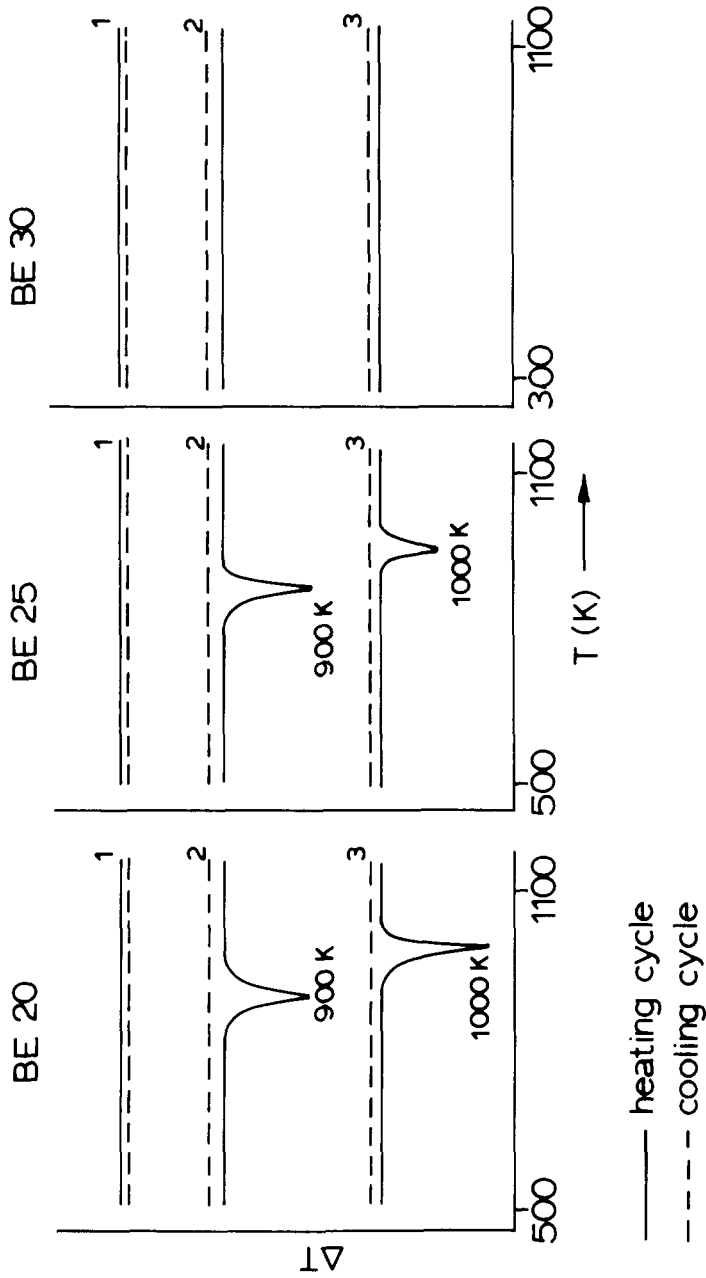


FIG. 1
Differential thermal analysis of samples after various heat treatments
1. Fresh samples; 2. Samples heated at 775 K for 500 hours; 3. Samples heated at 900 K for 500 hours.

shown in Fig.1. Thermal analyses of fresh sintered pellets do not show any DTA peak. After annealing at 775 K for 500 hours however, BE20(PA) and BE25(PA) show endothermic peaks in DTA at 900 K. No peaks were observed for BE30(PA).

After annealing at 900 K for 500 hours a different endothermic peak at 1000 K is observed. Its intensity decreases with decreasing annealing time (8). No further changes could be observed in the cooling or subsequent heating cycles. Obviously the transitions seen in DTA at 900 and 1000 K are caused by the long term annealing. When DTA was recorded after reheating BE20(PB) and BE25(PB) at 1025 K for 50 hours the transition at 1000 K disappeared. None of the above transitions could be observed on BE30 samples.

The transitions at 900 and 1000 K were not accompanied by weight changes in the DTG measurements and hence correspond to phase transformations. The heating/cooling times used in DTA are much too short to introduce such a transformation again; only long term annealing can cause this.

ii. Structural studies

As expected BE20, BE25 and BE30 ceramics sintered at 1125 K, crystallize in the cubic fluorite structure. After annealing at 900 K for 500 hours the X-ray diffraction diagrams of BE20(PB) and BE25(PB) show the presence of an additional hexagonal (rhombohedral) phase. **The strong lines of the hexagonal phase**, found in the X-ray diffraction diagram of BE20, are given in table 2. For the calculation of the cell parameters the weak lines (not given in table 2) have also been used. The cell parameters for the hexagonal phase are $a = 0.39454(2)$ nm and $c = 2.7237(3)$ nm for BE25 and $a = 0.39504(2)$ and $c = 2.7274(3)$ nm for BE20. Both hexagonal phases belong to the space group $R\bar{3}m$, $Z=9$, (or $Z=3$ for the rhombohedral cell). The corresponding volumes for the hexagonal cell are 0.3686 nm³ and 0.3672 nm³ for BE20 and BE25 respectively. The volume shrinkage of about 1%, in comparison with the cubic cell, can give rise to stress build up during the phase transformation. This will be discussed later.

TABLE 2

X - ray powder diffraction data for the BE20 hexagonal phase, only the strong lines are given. Lines of the cubic phase are not included.

h	k	l	d(calc)	d (obs)	I(obs) %
0	0	1	0.3395	0.3390	31
0	1	2	0.3318	0.3313	25
1	0	4	0.3058	0.3053	100
0	0	9	0.3031	0.3026	65
0	1	5	0.2898	0.2895	58
0	1	8	0.2415	0.2412	14
1	1	0	0.19752	0.19737	29
1	0	13	0.17885	0.17880	18
0	2	4	0.16591	0.16548	27

After 500 hours of annealing of the cubic samples at 900 K, BE20(PB) and BE25(PB) contained about 80% and 20% of this hexagonal phase respectively.

Neutron diffraction studies have shown that the cubic bismuth erbium oxides have an additional short range ordering (11). Battle et al. (12,13) found ordered domains of hexagonal (rhombohedral) symmetry in these materials. It is known that stabilisation of bismuth oxide by higher rare earth oxides results in a rhombohedral structure. Takahashi et al. (14) suggested the existence of microdomains with a structure, which is correlated to the rhombohedral structure. Recently a hexagonal bismuth yttrium oxide has been reported (15). This phase has a layered structure in the space group $R\bar{3}m$ and could be prepared directly from the oxides by a solid state reaction. The hexagonal phase formed in the case of BE20(PB) and BE25(PB) shows a close similarity to this phase.

When the samples BE20(PB) and BE25(PB) were reheated at 1025 K for 50 hours, the samples contained only the cubic phase. The transition seen in DTA at 1000 K (Fig.1), corresponds therefore to a rapid change from hexagonal to cubic. This implies that on heating at 900 K the **slow** (>150 hours) cubic to hexagonal phase transition occurs and that the resulting hexagonal phase is stable up to 1000 K, where **rapid** conversion to the cubic phase occurs. The lower temperature limit, where the hexagonal phase forms, is not exactly known but is situated between 775 K (no hexagonal phase) and 900 K. Such phase changes were not observed in BE30(PB).

Traces of α - bismuth oxide were observed in the X-ray diffraction diagrams of BE20(A), BE25(A), BE20(B), BE25(B). The transformation at 900 K in DTA (Fig.1), seen only for samples annealed at 775 K for 500 hours, may correspond to a solid state reaction of the bismuth oxide with the solid solution, (which is still cubic, even after annealing at 775 K for 500 hours) to form the composition of the original solid solution again. Heating times used in DTA are much too short to introduce the hexagonal phase, which we found first after annealing at 900 K for at least 150 hours. The presence of α - bismuth oxide may point to a partial decomposition of the solid solution and hence raises a question on the reliability of the material for use. Absence of any such behaviour makes BE30 an ideal composition for use. Compositions between BE25 and BE30 are now under investigation .

iii. Mechanical studies

The mechanical and morphological properties of the samples are given in Table 3. The σ_f values are lower in comparison with those of cubic yttria - stabilized zirconia, but are quite acceptable, certainly for bismuth oxide based systems. Preliminary results in the system $Bi_2O_3 - Tb_2O_3$, produced with the coprecipitation method, show even higher σ_f values; up to 120 MPa. It is note worthy that the sintering temperature does not have a strong influence on the fracture strength of the samples. The solid state reaction yields samples, which are weaker than those obtained from coprecipitation.

TABLE 3
Properties of the ceramics after various treatments

Sample code	T _s + (K)	Phases present	Density (%)	Average grain size (μm)	σ _f (MPa) *
BE25(P)	1035	Cubic(fluorite)	97.2	5	79 ± 5
BE25(P)	1075	,,	98.4	7	89 ± 8
BE25(P)	1125	,,	99.3	15	79 ± 11
BE25(S)	1125	,,	98.0	10	57 ± 5
BE25(SA)	1125	Cubic+αBi ₂ O ₃	98.0	10	89 ± 3
BE25(SB)	1125	Cubic+Hexagonal	98.0	--	95 ± 12
BE25(P)	1125	} Cubic(silica contaminated)	98.0	--	40 ± 12
BE30(P)	1125				
ZY	1670	,,	93.5	4	162 ± 5

+ see table 1 for sample code; ++ Sinter temperature; * Three point bending strength(σ_f); ** 8.9 mole % Yttria - stabilized Zirconia(10).

The cubic to hexagonal phase transition does not seem to affect the strength of the samples. At these temperatures stress relaxation occurs rapidly in bismuth oxide based solid solutions (extended creep is observed) and consequently any stresses induced by the slow phase transition (volume change of 1.07 % for BE25) are probably relieved. Also no apparent effect of grain size on the mechanical strength is observable. As expected, silica contamination leads to weak samples due to the formation of a sillenite type structure, which extracts large amounts of bismuth. This results in destabilisation of the surrounding matrix (8).

CONCLUSIONS

1. Coprecipitation as a method of preparation for Bi₂O₃ - Er₂O₃ ceramics and Bi₂O₃ - Tb₂O₃ ceramics results in relatively strong and machineable materials as compared to the solid state reaction method.

2. In case of samples containing up to 25 mole % of erbium oxide a slow cubic to hexagonal (rhombohedral) phase transformation is observed after heating at 900 K for an extended period. This hexagonal phase is stable up to 1000 K where it quickly transforms to the cubic phase. This hexagonal phase is assumed to nucleate from microdomains of the same structure present in these materials.

3. The lower temperature limit, where the hexagonal phase forms after long term annealing, is situated between 775 K (no hexagonal phase) and 900 K.

4. Although the hexagonal phase introduces a volume contraction, it does not seem to affect the mechanical strength of the samples.

5. Heating at 775 K for extended times causes the

formation of traces of α - bismuth oxide, which may point to slow decomposition. The material itself however, remains cubic at this temperature.

6 . None of the above mentioned changes were observed in BE30 and hence this material is the better choice for application in oxygen pump and - sensor devices in spite of the lower conductivity.

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REFERENCES

1. M.J.Verkerk, and A.J.Burggraaf, Solid State Ionics, 3/4, 463, (1981).
2. I.C.Vinke, K.Seshan, K.J. de Vries, B.A.Boukamp and A.J.Burggraaf, Electrochemical properties of ceramic Bi_2O_3 - Er_2O_3 solid solutions, Solid State Ionics (to be published).
3. I.C.Vinke, K.Seshan, B.A.Boukamp, K.J. de Vries and A.J.Burggraaf, The electrochemical influence and oxygen exchange properties of mixed conducting electrode materials on solid oxide electrolytes, Proceedings of 6th Int. Conf. on Solid State Ionics at Garmisch Partenkirchen, Sep,6-11,1987, to be published as special issue of Solid State Ionics 1988.
4. M.J.Verkerk and A.J.Burggraaf, J. Electrochem. Soc., 128, 75 (1981).
5. T.Takahashi, T.Esaka, and H.Iwahara, J.Appl. Electrochem., 5, 197 (1975).
6. H.A. Harwig and A.G. Gerards, J. Solid State Chem., 26, 265 (1978).
7. M.J. Verkerk, K. Keizer and A.J. Burggraaf, J. Appl. Electrochem., 10, 81 (1980)
8. H.Kruidhof, K.Seshan, B.C.Lippens Jr., P.J.Gellings and A.J.Burggraaf, Mater. Res. Bull., (in press).
9. G.De With and N.Hattau, J. Mater Sc., 16, 841 (1981).
10. K.Keizer, A.J.Burggraaf and G.De With, J. Mater Sc., 17, 1095 (1982)
11. M.J.Verkerk, G.M.H. van de Velde, A.J.Burggraaf and R.B.Helmholdt, J. Phys. Chem. Solids, 43, 1129 (1982).
12. P.D.Battle, C.R.A.Catlow, J.W.Heap and L.M.Moroney, J. Solid State Chem., 63, 8 (1986).
13. P.D.Battle, C.R.A.Catlow, and L.M.Moroney, J. Solid State Chem., 67, 42 (1987).
14. T.Takahashi and H.Iwahara, Mater. Res. Bull., 13, 1447 (1978)
15. A.Watanabe and K.Kikuchi, Solid State Ionics, 21, 287 (1987).