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YTTRIA-STABILIZED BISMUTH OXIDE DENSE SOLID ELECTROLYTE PREPARED BY SPARK PLASMA SINTERING

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Single phase $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ samples with x = 0.15, 0.20, 0.25 and 0.30 were successfully synthesized via conventional solid state method at the calcination temperature of 800 °C for 16 h. These samples crystallized in cubic fluorite structure, space group Fm-3m and lattice parameter of 5.527< a < 5.464 Å. $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ subsolidus system was thermally stable as no phase transition or weight loss was discernible within the studied temperature. Dense samples were sintered by both Spark Plasma Sintering (SPS) and pressureless sintering. $(Bi_2O_3)_{0.80}(Y_2O_3)_{0.20}$ samples with relative density higher than 94 % and different grain sizes were obtained.

Introduction

Functional ceramics based on stabilized δ-Bi_2O_3 with high oxygen ion conductivity have been attracting interest because of their potential applications in solid oxide fuel cells (SOFC), oxygen pumps, electrochemical sensors and oxygen-permeable membrane catalysts. However, this δ phase is only stable in a narrow temperature range (730 °C to 830 °C), limited by an abrupt phase transition and its melting point. According to the literature, the Y_2O_3-doped Bi_2O_3 system exhibits high conductivity of oxygen ions and may be a promising solid electrolyte material for more extensive applications [1-4]. The ionic conductivity of the electrolyte is related to the microstructure and sample density. It was demonstrated that there exists a linear relationship between the sample relative density and the intergranular conductivity [5]. A proper sintering method is essential to prevent the crystal grain growth.

Methodology

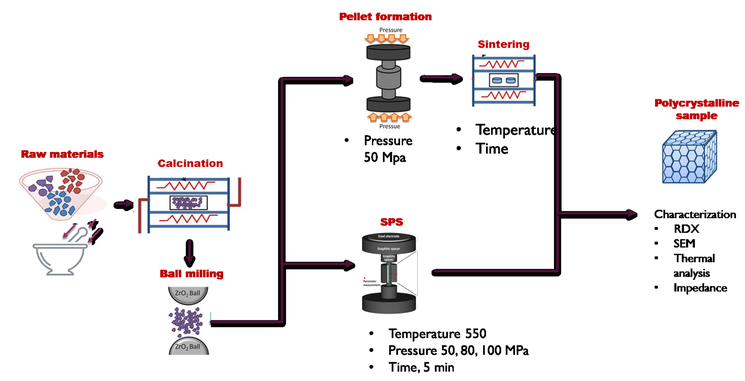


Figure 1. Synthesis of $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ samples

Results

Phase formation of solid solution $(Bi_2O_3)_{1-x}(Y_2O_3)_x$

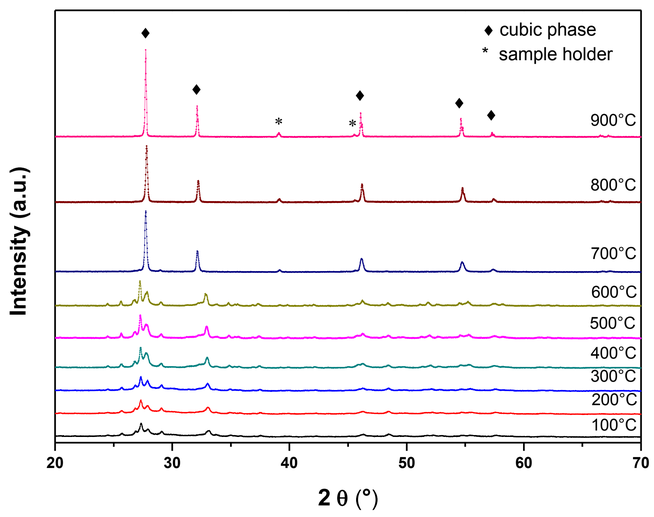


Figure 2. High temperature XRD patterns of $(Bi_2O_3)_{0.80}(Y_2O_3)_{0.20}$ sample

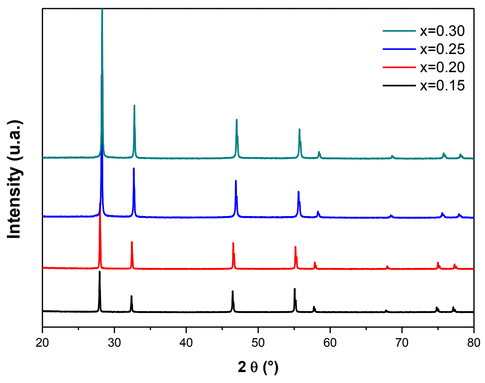


Figure 3. XRD patterns of prepared $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ samples in the range of 0.15≤ x ≤ 0.30

The formation of single phase samples is confirmed by the absence of characteristic XRD lines of the constituent oxides and other phases in the XRD diffraction patterns. It is found that solid solution $(Bi_2O_3)_{1-x}(Y_2O_3)_x$, where x = 0.15, 0.20, 0.25 and 0.30, crystallized in face centered cubic with lattice parameters of 5.527< a < 5.464 Å with space group Fm-3m.

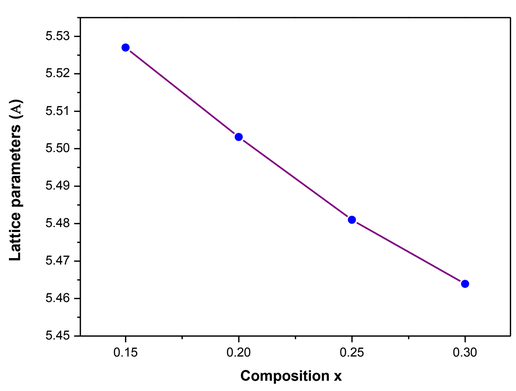


Figure 4. Variation of lattice parameter as a function of the composition in $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ solid solution

The linear-plot obeyed Vegard's law, revealing a well-behaved substitutional solid solution existed within the incorporated dopant concentration range.

Thermal analysis

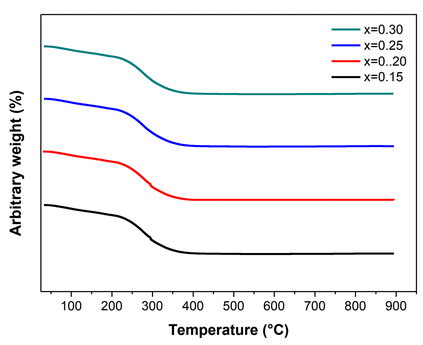


Figure 5. Combined TGA thermograms of $(Bi_2O_3)_{0.8}(Y_2O_3)_{0.2}$ solid solution

Horizontal lines across the heating temperature range are observed in all the samples, showing no any systematic weight change occurred when the samples are heated up to 900 °C

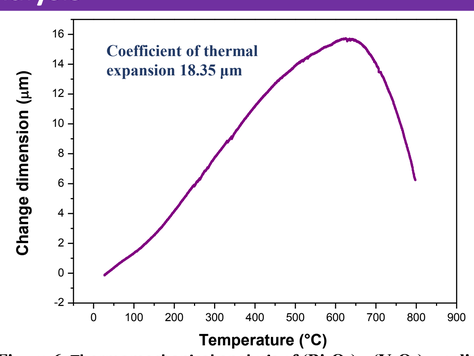


Figure 6. Thermomechanical analysis of $(Bi_2O_3)_{0.8}(Y_2O_3)_{0.2}$ solid solution

With the aim to define the adequate temperature for sintering, a TMA was carried out on a green pellet of $(Bi_2O_3)_{0.8}(Y_2O3)_{0.2}$. It can be seen that the shrinkage started from 650 °C, and the maximum shrinkage rate was observed around 700 °C.

Microstructure

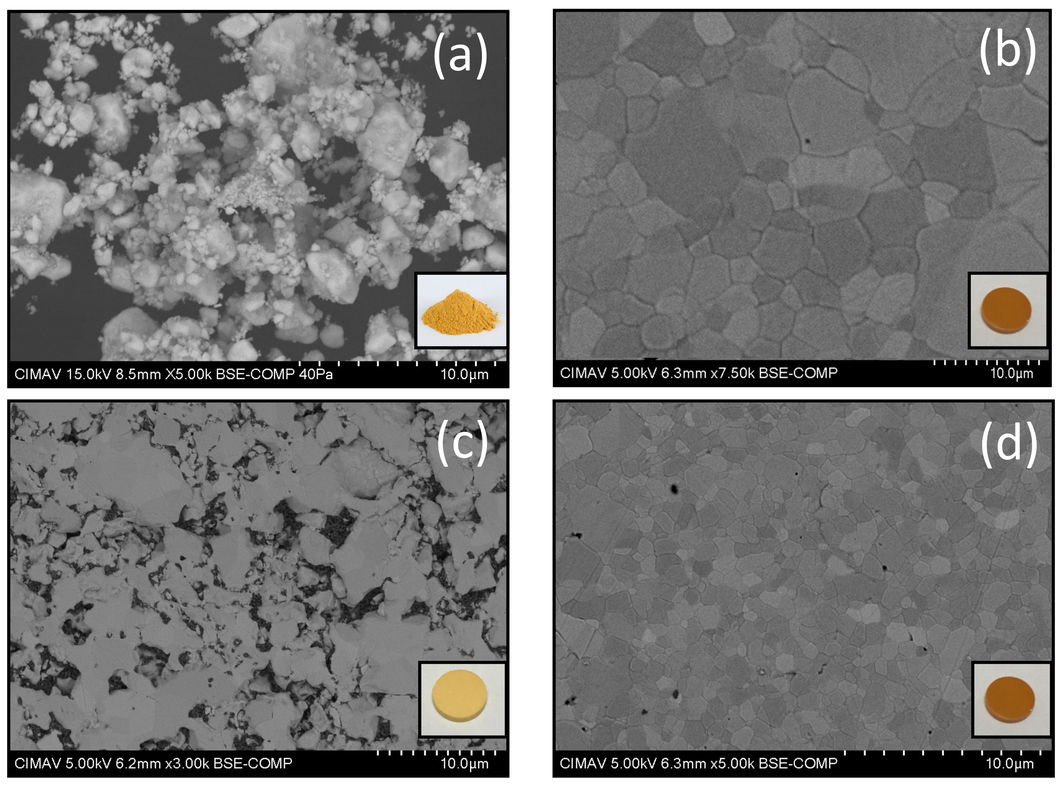


Fig. 7. Microstructure of $(Bi_2O_3)_{0.80}(Y_2O_3)_{0.20}$ samples. (a) as-milled, (b) presureless sintered at 800 °C/8 h, (c) SPS at 600 °C/1 min, and (d) SPS at 750 °C/1 min

	Sample	Grain size (µm)	Relative density (%)
Pressureless sintering	750 °C 8 h	5.9	89.3
	800 °C 8 h	6.1	93.2
	900 °C 8 h	8.5	94.8
SPS	750 °C 1 min	0.8	96.2

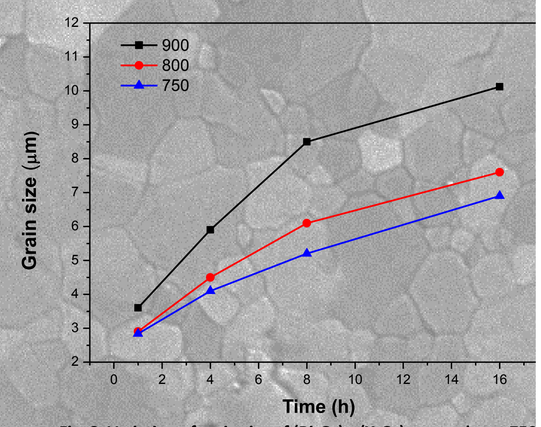
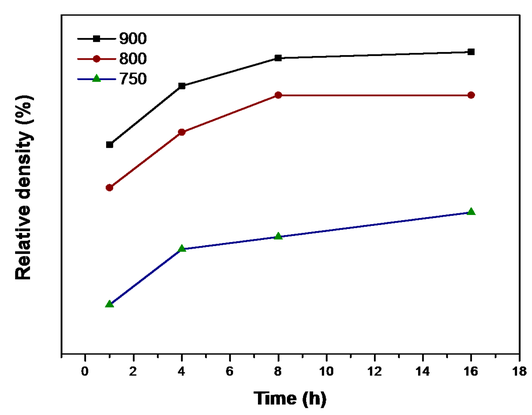


Fig. 8. Variation of grain size of $(Bi_2O_3)_{0.8}(Y_2O_3)_{0.2}$ samples at 750 °C, 800 °C and 900 °C as a function of sintering time



at 750 °C, 800 °C and 900 °C

Conclusions

Substitutional solid solution was confirmed at 0.15 ≤ x ≤ 0.30 together with a decrease in lattice parameter with higher Y_2O_3 content. The cell shrinkage was attributed to the replacement of larger Bi^{3+} cation with smaller Y^{3+} cation. Dense samples with close relative densities of about 96% and grain size varying from 0.8 to 8.5 µm were successfully prepared by SPS and pressureless sintering.

References

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