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The effects of zirconia addition on sintering behavior, mechanical properties and ion conductivity of BICUVOX.1 material

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Abstract

The present work focuses on the effects of microstructural modifications in terms of grain size, and incorporation of zirconia as a second phase on the sintering behavior, mechanical properties and ion conductivity of $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ material. The mentioned properties have been determined by impedance spectroscopy, fracture toughness, and microhardness tests. The incorporation of ZrO_2 (less than 1 wt.%) increase the optimum sintering temperature, results in reducing the grain size of the sintered samples and leads to more than 15% improvement in the studied mechanical properties. On the other hand, the ion conductivity is slightly reduced at low temperature, which is probably due to high density of grain boundaries in the samples containing ZrO_2.

Keywords: BIMEVOX; Composites; Impedance; Ionic conductivity; Mechanical properties

1. Introduction

$Bi_2V_{1-x}Me_xO_{5.5-3x/2}$, Me, which stands for the substituting metal cation (e.g. Cu, Co, Ni, Ti,...) and x is the molar substitution of the metal cation for vanadium, family of solid electrolytes possessing high oxide–ion conductivity at moderate temperatures and also catalytical activity towards oxygen dissociation, was reported recently as one of the best candidates for the membranes of ceramic oxygen generators (COG).[1,2] For optimizing COG, the mechanical properties of the membrane are important as well as the ion conductivity and electrochemical properties. If it were possible to reduce the thickness of the membrane, by using a material exhibiting high strength, the efficiency of the oxygen production could be improved.

In the present research we examined the effects of addition of a small amount of submicron zirconia particles to the $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ (a member of the BIMEVOX family with the highest ion conductivity)[3–5] on the sintering behavior, microstructure, ion conductivity and mechanical properties.

2. Experimental procedure

Polycrystalline $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ samples were synthesized from analytical grade of Bi_2O_3, V_2O_5, and CuO. The reactants were thoroughly mixed in an agate mortar and calcined at 650°C for 15 h and then at 750°C for 5 h in air with two intermediate grindings. The crystal structure of the synthesized compound was identified by means of X-ray diffraction using CuK_α source. Milling was performed for 20 h (using zirconia balls with 3 mm diameter).

In the case of the samples containing 0.5 and 1 wt.% ZrO_2, appreciate amount of 3-mol% Y_2O_3-stabilized ZrO_2 (Tosoh, Tokyo, Japan), 30 nm particle size, was dispersed by ultrasonic vibration and then mixed with BICUVOX.1 powders using wet ball-milling for 30 h. The powder samples (0.6 g portions) were pressed into disc compacts at the hydrostatic pressure at 350 MPa. For mechanical property measurements 3×4×33 mm rods formed. To determine the optimum sintering conditions, the green samples were sintered at the

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temperature and time ranges of 680 to 760°C and 5 min to 20 h, respectively, in air. The density of disc compacts was measured in isobutyl alcohol. The samples thermally etched at 650°C for 2 h, and the microstructures were analyzed on field emission scanning electron microscope (FE–SEM, Jeol JSM-6340F). For measurements of the micro-hardness and fracture toughness, the samples were polished with a 0.5 μm diamond paste. The micro-hardness and fracture toughness were performed by the means of Vickers' test method (Akashi, AVK-C1) and three-point bending test (Shimadzu, auto graph AG-10TA) of the notched samples (Japanese Industrial Standard, JIS Z 8401), respectively. The three-points bending tests were carried out with a span of 16 mm at a cross-head speed of 0.5 mm/min. Oxide ion conductivity was measured in air by means of a two-probe ionic ac technique by using impedance spectroscopy (Model 1260, Solarton). Pt electrodes were sputtered on both sides of the samples. The conductivity measurement's cell was housed in a quartz–glass tube equipped by an electrical furnace, and artificial air was fed into the tube. The ion conductivities were measured in the frequency range of 0.1 to 1 MHz and from 100 to 450°C.

3. Results and discussion

3.1. Powder characterization

From the XRD analyses, taken at room temperature, it was found that the BICUVOX.1 and composite samples have γ crystal structure of the parent compound ($Bi_4V_2O_{11}$), and addition of zirconia in the range of 0 to 1 wt.% does not change the crystal structure or even the cell parameters, calculated by a least squares cell refinement program[6] and shown in Table 1, which indicates that the zirconia particles have not been incorporated in the crystal structure of the base compound and just act as a second phase.

3.2. Sintering behavior and microstructural characterization

The sintering behavior of the BICUVOX.1 sample and those containing 0.5 and 1 wt.% ZrO_2 are presented in Figs. 1 and 2. The variation of the density of the samples sintered at different temperatures for 5 h is shown in Fig. 1. The density of BICUVOX.1 increased with the increase of sintering temperature and reached maximum value (96% of theoretical density) at 730°C. At higher temperatures, a reduction in the density was observed, which could be due to the inhomogeneous grain growth, inducing strain and cracks in the sample microstructures.[7] Thus, the optimum sintering temperature was estimated to be 730°C. On the other hand, the optimum sintering temperature of the samples containing ZrO_2 was slightly higher than that of the pure ones, about 750 to 760°C. Fig. 2 shows the variation of the density and grain size of the pure and the samples containing ZrO_2 sintered at 730°C as a function of sintering time. The addition of ZrO_2 keeps the grain size small ($d < 2$ μm) while the density increases with sintering time. In the case of pure BICUVOX.1 samples, the grain size increases and reaches 20 μm after 1500 min of

Table 1
Cell parameters of BICUVOX.1 and BICUVOX.1 + 1 wt.% ZrO_2

Compound	Lattice parameters (A°)		Crystal structure
	a	*c*	
$Bi_2V_{0.9}Cu_{0.1}O_{5.35}$	3.916	15.427	γ, tetragonal
$Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ + 1 wt.% ZrO_2	3.914	15.43	γ, tetragonal

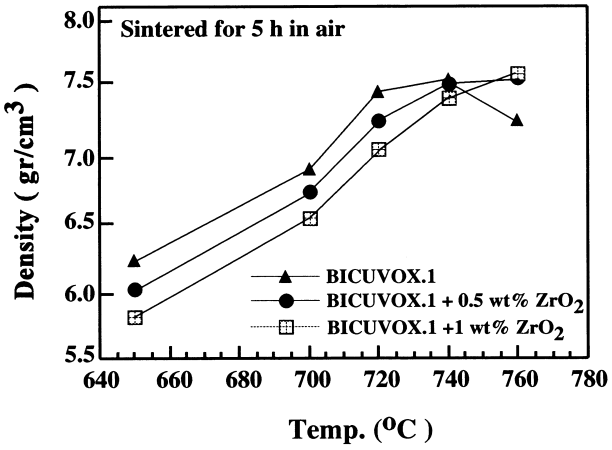

Fig. 1. Variation of the density of BICUVOX.1 and BICUVOX.1 containing 0.5 and 1 wt.% ZrO_2 as a function of temperature (sintering time = 5 h).

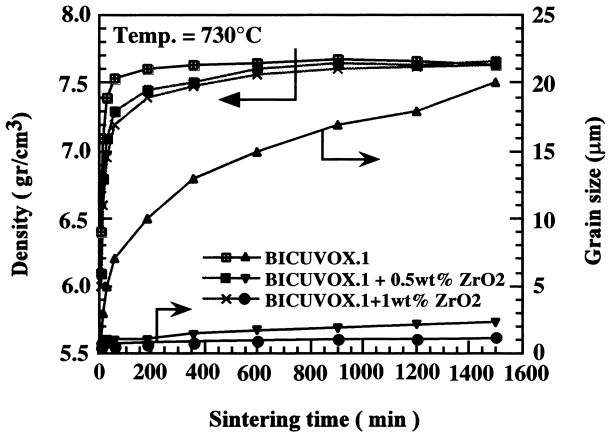

Fig. 2. Variation of the density and grain size of BICUVOX.1 and BICUVOX.1 containing 0.5 and 1 wt.% ZrO_2 as a function of sintering time (sintering temperature = 730°C).

sintering. We suggest that the ZrO_2 particles grain growth inhibition effect is responsible for the difference in optimum sintering temperature. In other words, it is expected that the inhomogeneous grain growth would be postponed to the higher temperatures by addition of zirconia particles, which means that sintering can be carried out at higher temperature without the unfavorable effect of inhomogeneous grain growth. The microstructure of the pure samples and those containing 0.5 and 1 wt.% zirconia, sintered at 730°C for 10 h, are shown in Fig. 3. The micrographs clarify that the grain size of the samples containing ZrO_2 are smaller than the pure sample.

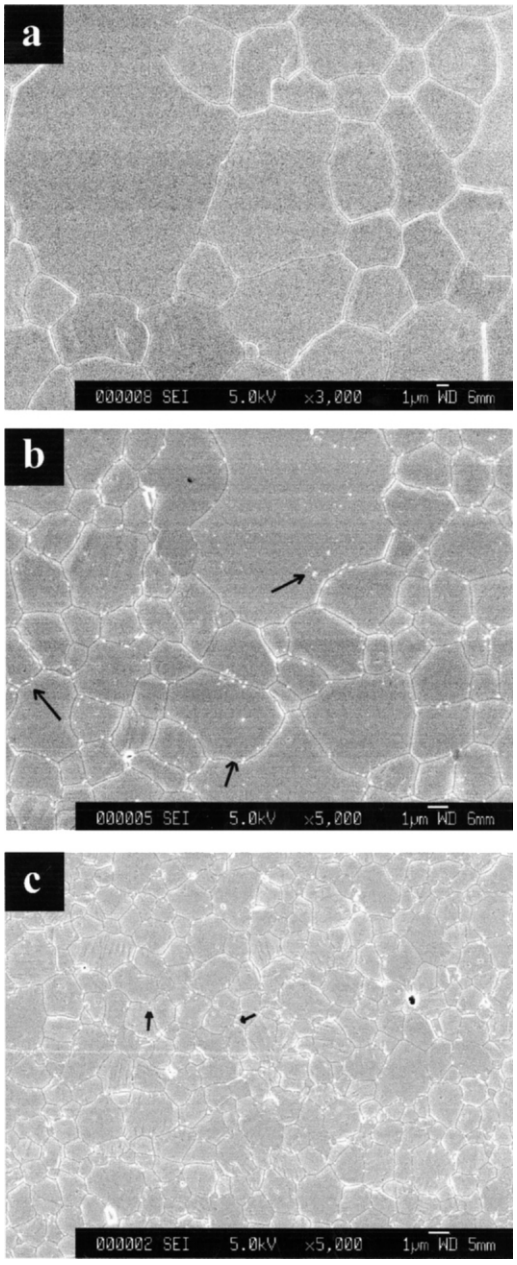

Fig. 3. SEM microstructures of: (a) BICUVOX.1; (b) BICUVOX.1 + 0.5 wt.% ZrO_2; (c) BICUVOX.1 + 1 wt.% ZrO_2 sintered at 730°C for 10 h, arrows indicate ZrO_2 particles.

3.3. Mechanical properties

Fig. 4 illustrates the variation of fracture toughness and micro-hardness of BICUVOX.1 samples as a function of zirconia content. Addition of even a small amount (0.5–1 wt.%) of zirconia shows a clear effect of improving the mechanical properties, which is due to the different grain size of the single and two phase samples. We suggest that the most important toughening mechanisms is probably crack deflection at the grain boundaries,[8] as also has been reported for 8YSZ/SiC nanocomposites solid electrolyte.[9] Further investigation is going to be carried out on these details.

3.4. Ion conductivity characterization

Nyquist plots of BICUVOX.1 and of the samples containing 0.5 and 1 wt.% ZrO_2 measured at 150°C are shown in Fig. 5. The plots for the samples containing

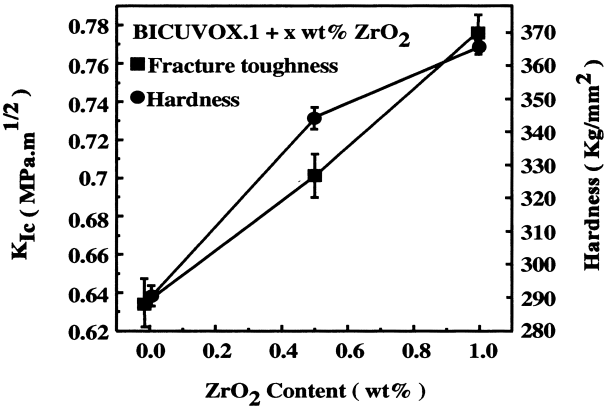

Fig. 4. Fracture toughness and micro-hardness of BICUVOX.1 and BICUVOX.1 containing 0.5 and 1 wt.% ZrO_2, sintered at 730°C for 10 h.

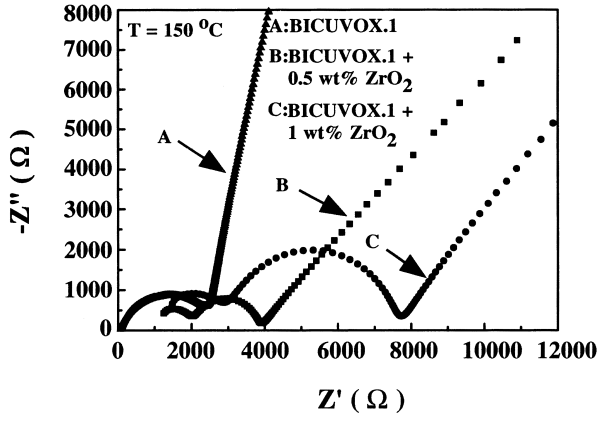

Fig. 5. Impedance spectra of BICUVOX.1 and BICUVOX.1 containing 0.5 and 1 wt.% ZrO_2 sintered at 730°C for 10 h, at 150°C.

Table 2
Conductivities and activation energies of BICUVOX.1 and the samples contaning 0.5 and 1 wt.% ZrO_2 in respective temperature ranges

Sample type	Conductivity x 10^3 (S.K/cm)			Activation energy (eV)
	200 °C	300 °C	400 °C	100 < T < 400 °C
BICUVOX.1				
Total conductivity	0.408	5.4	32	0.63
BICUVOX.1+0.5 wt%□rO$_2$				
Bulk	0.54	5.1	30.6	0.62
Grain boundary	0.72	14.8	-----	0.745
Total	0.31	4	26	0.673
BICUVOX.1+ 1wt%□rO$_2$				
Bulk	0.5	5.2	30	0.613
Grain boundary	0.41	8.3	----	0.75
Total	0.22	3.2	23	0.683
BICUVOX.1				
Total conductivity				
Ref (4)	0.4	-----	19	0.6
Ref (10)	0.12	1.8	11.4	0.666
Ref (12)	-----	3.2	-----	-------

ZrO_2 show two semicircles attributed to the grain boundary and bulk contributions to the total impedance, but for the pure BICUVOX.1 sample with large grain size ($d > 20$ μm), the effect of the grain boundary cannot be seen. In the case of composite samples, the contribution of the grain boundaries is higher, which is due to the higher density of the grain boundaries.

The values of conductivities and corresponding activation energies for pure and those containing ZrO_2 are summarized in Table 2. The activation energy for ionic conduction of the pure BICUVOX.1 is the same as reported by Dygas et al.[10–11] and Pernot et al.[12] However, the conductivity, especially at lower temperature, is higher than the values of the previous reports, which could be due to the different powder processing and sintering conditions which led to different microstructural characteristics. On the other hand, the conductivity and activation energy of the bulk for all the samples tested were obtained in the same level. In the case of composite samples, the density of the grain boundaries is higher and as a result their contribution in the total conductivity is also more, which causes a reduction in the total ion conductivity with respect to the single phase BICUVOX.1 samples. Anyway, it is noteworthy that by increasing the temperature the resistivity of the grain boundaries reduces faster than that in the bulk,[10] so that the contribution of the grain boundaries in total ion conductivity is less pronounced and as shown in Fig. 6, the total ion conductivity of different samples at high temperature is more similar.

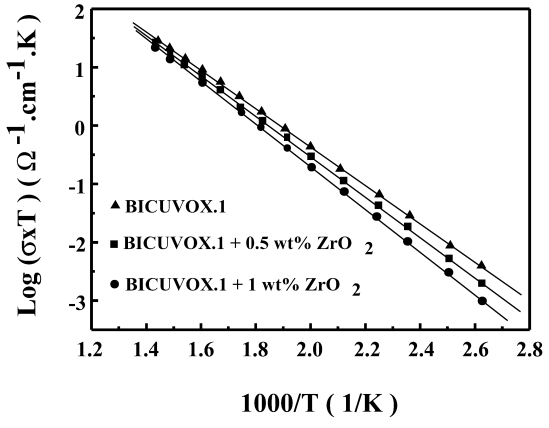

Fig. 6. Arrhenius plots for BICUVOX.1 and BICUVOX.1 containing 0.5 and 1 wt.% ZrO_2 sintered at 730°C for 10 h.

4. Conclusions

The effects of addition of 0.5 and 1 wt.% submicron zirconia to BICUVOX.1 were examined. The following conclusions were drawn from the present study.

1. Addition of 0.5 to 1 wt.% ZrO_2 to BICUVOX.1 is effective to keep the grain size small during sintering and lead to an improvement in mechanical properties, so that the microhardness and fracture toughness increase more than 15% as compared with those of BICUVOX.1. On the other hand, it slightly reduces the conductivity, which is less pronounced at high temperature.
2. By using high strength BICUVOX.1/0.5–1 wt.% ZrO_2 composites as the membrane of a ceramic oxygen generator it would be possible to reduce the thickness of the membrane and increase the efficiency of the device.

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