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BICOVOX: Sintering and Grain Size Dependence of the Electrical Properties

M. C. Steil,[a†] J. Fouletier,[a*] M. Kleitz[a] and P. Labrune[b]

[a]Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (L.E.P.M.I.), INPG and CNRS, BP 75-38402 Saint-Martin d'Hères Cédex, France
[b]Air Liquide, Centre de Recherches Claude Delorme, BP 126, Les Loges en Josas, 78354 Jouy-en-Josas Cédex, France

Abstract

The sintering conditions and the effects of the mean grain size on the electrical properties of cobalt-substituted bismuth vanadate ($Bi_2V_{0.9}Co_{0.1}O_{5.35}$), *referred to as BICOVOX, have been studied. The influence of the experimental conditions (sintering temperature and duration, oxygen partial pressure) on the resulting density of the pellet was evaluated by dilatometric measurements. The grain size dependence of the electrical properties was studied by impedance spectroscopy. It is shown that the BIMEVOX characteristic hysteresis, which results in a significant decrease of the ionic conductivity below about 450°C, is suppressed provided that the grain size is small enough. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: BICOVOX, grain growth, sintering, grain size, impedance.

1 Introduction

Although stabilized zirconia is used in most applications of solid oxide electrolytes, efforts are being made to synthesize other materials exhibiting higher O^{2-} conductivity at medium temperatures. As an alternative, ceria- and bismuth oxide-based solid solutions have been investigated. Due to the easy reduction of these oxides, their use is restricted to applications involving fairly high oxygen pressures, such as oxygen pumping.

The family of so-called BIMEVOX compounds,[1] with formula $Bi_4V_{2-x}Me_xO_{11-\delta}(0 \leq x \leq 2)$, appears to be the most attractive for applications below 500°C, where ionic conductivity is the determining parameter. These compounds are derived from $Bi_4V_2O_{11}$ in which vanadium (and/or bismuth) is partly replaced by iso- or aliovalent cations of different sizes and valence states, i.e., Li^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Ge^{4+}, Sn^{4+}, Pb^{4+}, Nb^{5+}, etc. These substitutions stabilize the γ-phase which exhibits a high ionic conductivity associated with a small activation energy.[2,3] The electrical conductivity anisotropy of BIMEVOX single crystals and the electronic conductivity variation with oxygen pressure, which are also determining parameters, have now been documented.[4,5]

The value of the electrical conductivity appears to be independent of the thermal history only at temperatures higher than 560°C. For lower temperatures, it has been reported that the electrical conductivity of single crystals and sintered pellets varies when the BIMEVOX material is kept at high temperature for various periods of time.[6,7] The decrease of the electrical conductivity with time, between 300 and 480°C, has been ascribed to a slow ordering in the conducting γ-phase. The grain size has been suggested to have an effect on the extent of the hysteresis.[8] In spite of the importance of such a behavior, which may induce serious limitations for practical applications, only a few works have been carried out on the sintering process and the resulting pellet density and microstructure.[8–10]

This paper is devoted to the study of the relationship between the electrical properties of BICOVOX sinters and their microstructure.

2 Experimental

BICOVOX powder was synthesized at the L.C.P.S. (Villeneuve d'Ascq) by the conventional solid state reaction method from stoichiometric amounts of dried oxides (Bi_2O_3, V_2O_5 and CoO) to obtain the

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[*] To whom correspondence should be addressed. Fax: +33-4-7682-6670; e-mail: jacques.fouletier@lepmi.inpg.fr

[†] Present address: Laboratoire de Cristallochimie et Physico-Chimie du Solide, ENSCL, BP 108, 59652 Villeneuve d'Ascq Cedex, France.

composition $Bi_2V_{0\cdot9}Co_{0\cdot1}O_{5\cdot35}$.[11] The oxide was ground in an agate mortar and fired in a gold foil boat for 12 h successively at 600, 700 and 800°C. The compound was then cooled at 20°C/h.

The powder was ground by attrition (Netzsch PR 015) using zirconia balls (1–2 mm in diameter). The optimized attriting conditions were: a 40 wt.% suspension of BICOVOX powder in ethanol, 450 rpm, for 4 h. After this attrition, the particle mean size, estimated by SEM and laser analysis, was less than 0·5 μm.

Pellets were pre-pressed uniaxially (10 mm in diameter and 3–5 mm in thickness), then pressed isostatically under various pressures. Sintering conditions were optimized by using dilatometric measurements (Adamel D124 dilatometer) with the following temperature cycle conditions: heating at 120°C/h, maximum temperature 820°C, holding time at maximum temperature 3 h, cooling at 120°C/h.

The powder shrinkage was also studied as a function of the green density (pellet sizes: 7 mm in diameter, 6 mm in thickness) and the sintering oxygen partial pressure (pellet sizes: 10 mm in diameter and 10 mm in thickness).

3 Results and Discussion

3.1 Sintering

Figure 1 compares the dilatometric curves obtained with pellets pressed isostatically at 150 MPa (green relative density: 60%) and 400 MPa (green relative density: 70%), respectively. The relative densities were calculated using the theoretical density, i.e., 7·77 g cm^{-3}.[12] The shrinkage starts for both samples at about 500°C. The samples can be considered as dense, respectively, at 800°C with a final shrinkage of 14·5% (isostatic pressing: 150 MPa) and at 720°C with a final shrinkage of 10·5% (isostatic pressing: 400 MPa).

The relative density after sintering at 750°C for 2 h was higher than 97% whatever the isostatic pressure (between 50 and 400 MPa). Note that such a high density has never been obtained using powders resulting from conventional syntheses, without attrition. To obtain a nearly full density, the mean grain size of the powder has to be smaller than 0·5 μm.

The influence of the oxygen partial pressure on the sintering process has been also observed on pellets isostatically pressed at 400 MPa. The dilatometric curves plotted under three atmospheres, i.e., pure oxygen, air and argon (oxygen mole fraction of a few 10^{-6}) are given in Fig. 2(a). The shrinkage starts at lower temperatures when the oxygen pressure is higher. Dense pellets are obtained at 720°C under pure oxygen and at 760°C under low oxygen partial pressure. This behavior could be related to the electrical conductivity variation of BICOVOX compounds with the oxygen pressure.[4] It has been shown previously that BICOVOX exhibits a *p*-type conductivity for oxygen pressures higher than 10^{-4} bar. Another feature of the curve plotted for argon is small expansion for temperatures higher than 780°C. As shown in Fig. 2(b), at 820°C, expansion was noticeable in argon (1·4%) and detectable in air (0·8%). No expansion was observed under pure oxygen for annealing times smaller than 3 h.

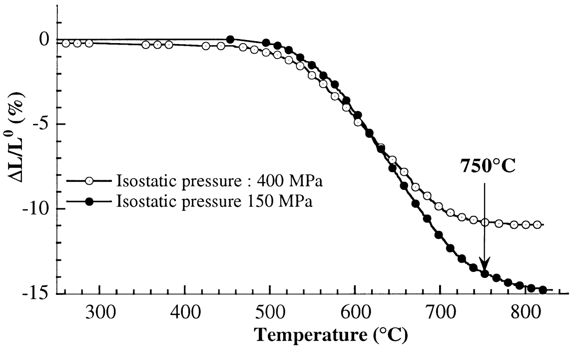

Fig. 1. Dilatometric curves obtained with BICOVOX pellets pressed isostatically at 150 MPa and 400 MPa.

The consequence of long sintering times, in air, has also been studied. Table 1 sums up the sample densities for four sintering temperatures. The mean densities have been calculated, from three identical runs, using two methods, i.e., from the pellet masses and sizes (referred as d_1 in Table 1) and using He picnometry (referred as d_2 in Table 1). As shown in Table 1, the density d_1 decreases slightly for sintering temperatures higher than 780°C, with a noticeable decrease at 820°C. The density d_2 obtained by He picnometry increases up to 780°C and remains close to 97% for higher temperatures. The densities d_1 and d_2 are identical for sintering temperatures lower than 780°C. The difference between d_1 and d_2, at higher sintering temperatures, can be explained by either an open porosity or cracks in the sample. SEM analyses on polished samples did not indicate differences of the open porosity for sintering temperatures lower than 820°C. Under these conditions, the abrupt lowering of the relative density d_1 can be due to crack formation within the sample. As shown on the SEM micrograph in Fig. 3, cracks are present in the pellet sintered at 820°C for 3 h. This could be ascribed to the anisotropy of the BIMEVOX materials which may grow more rapidly along certain crystallographic planes. Above a critical size of the platelet-shaped grains, excessive strain may be induced resulting in the observed cracks.

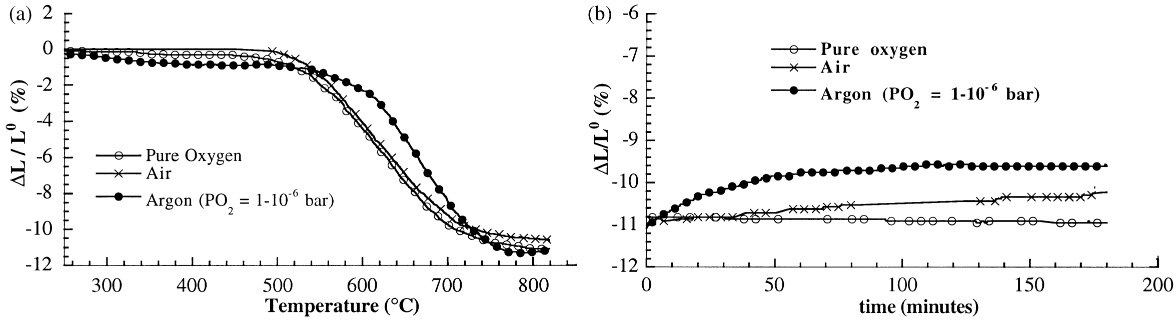

Fig. 2. (a) Dilatometric curves as a function of the oxygen partial pressure (isostatic pressing: 400 MPa). (b) Sample expansion versus time, at 820°C.

Table 1. Pellet densities after long sintering times

T (°C)	*Sintering times (h)*	*Density d_1 ($g\,cm^{-3}$) (from mass and sizes)*	*Relative density (%)*	*Density d_2 ($g\,cm^{-3}$) (He picnometry)*	*Relative density (%)*
750	6	7·40 ± 0·04	95·5	7·43 ± 0·02	95·9
780	6	7·42 ± 0·04	95·7	7·52 ± 0·02	97·0
800	6	7·33 ± 0·04	94·5	7·49 ± 0·01	96·6
820	3	6·92 ± 0·04	89·3	7·54 ± 0·01	97·3

3.2 Electrical properties

The influence of the sintering conditions on the electrical properties was studied by impedance spectroscopy (Hewlett–Packard impedancemeter, HP 4192) on symmetrical cells (10 mm in diameter and 3–5 mm in thickness) with painted gold electrodes (Degussa M 8001).

Arrhenius plots of the sample conductivities are given in Fig. 4 for two sintering conditions, i.e., 750°C for 30 min (grain size: 5–10 μm) and 800° for 12 h (grain size: 30–60 μm), in a pure oxygen atmosphere.

As shown in Fig. 4, the sample sintered at high temperature shows the usual thermal hysteresis: the electrical conductivity when heating is always lower than the values during subsequent cooling. Such a behaviour has often been observed for BIMEVOX materials.[6,7,9,13] It has been shown that this hysteresis is dependent on the dopant concentration[14] and is more significant with BIMEVOX single crystals[6] or with pellets prepared from coarse-grained powders.[9] Moreover, conductivity variations are often observed at constant temperature in the range 410 to 520°C.[7,15]

On the other hand, as shown in Fig. 4, no hysteresis is detected on the sample sintered at 750°C. Only a change in activation energy was observed: 0·64 eV at low temperatures and 0·37 eV for temperatures higher than 430°C. Moreover, the sample conductivity was reproducible on thermal cycling.

The hysteresis phenomenon is ascribed in the literature to an ordered structure (referred to as γ'), less conductive than the γ-tetragonal phase, which

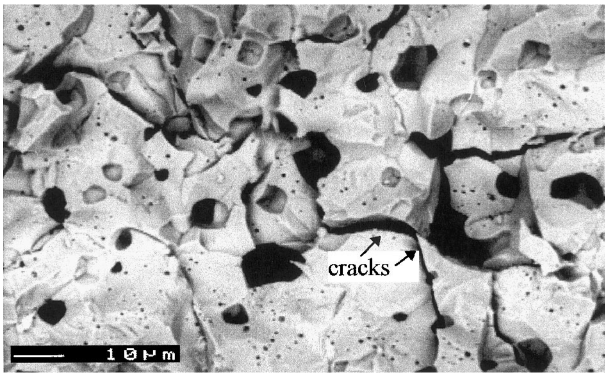

Fig. 3. SEM micrographs of a pellet sintered at 820°C for 3 h.

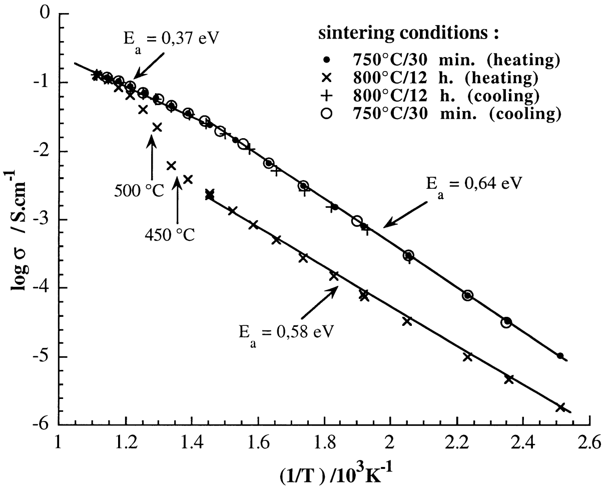

Fig. 4. Arrhenius plot of the electrical conductivity for two BICOVOX pellets sintered, respectively, at (a) 750°C for 30 min and (b) 800°C for 12 h.

develops slowly at medium temperature. This work demonstrates that the ordered structure does not appear over a long period of time provided that the grain size after sintering remains lower than a few μm. A small grain size stabilizes the highly conducting non-ordered γ-phase.

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