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Effect of Niobium doping on structural, thermal, sintering and electrical properties of $Bi_4V_{1.8}Cu_{0.2}O_{10.7}$

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Abstract

Doping $Bi_4V_{1.8}Cu_{0.2}O_{10.7}$ with niobium has led to the formation of the $Bi_4V_{1.8}Cu_{0.2-x}Nb_xO_{10.7+3x/2}$ solid solution. X-ray diffraction and thermal analysis have shown that only the compound with $x = 0.05$ presents a tetragonal symmetry with a γ' polymorph while the other compositions are of β polymorph. The influence of sintering temperature on the microstructure of the samples was investigated by the scanning electron microscopy (SEM). The ceramics sintered at temperatures higher than 820 °C present micro-craks. The evolution of the electrical conductivity with temperature and the degree of substitution has been investigated by impedance spectroscopy. Among all compositions studied the sample with $x = 0.05$ presents the highest value of the conductivity.

Keywords: Aurivillius phases; Ionic conductors; BIMEVOX materials; Solid electrolyte

1. Introduction

Since the discovery of the ferroelectricity in the Aurivillius compounds, after three years of the preparation of the first phase of the family [1], several laboratories throughout the world have been interested in these new materials [2–7]. Therefore, more than 70 new products have been synthesized and their ferroelectric properties studied. The structure of these phases consist of alternating $(Bi_2O_2)^{2+}$ layers and $(A_{n-1}B_nO_{3n+1})^{2-}$ groupments with perovskite-like sheets, built from edge-sharing octahedral. Generally, they obey the following formula: $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$ where A is a mono, di or trivalent ion and B a cation with average size and could be iron, aluminium, tungsten, etc., and n represents the number of perovskite-slabs.

The Aurivillius phases with higher n values are electrical insulators, and no publication dealing with the oxygen ionic conductivity has been reported in the literature, besides that published by Kendall et al. in 1994 [8] and which has been disputed thereafter by Snedden et al. [9]. This feature is due to the intolerance of this kind of Aurivillius phases to oxide ion vacancies. By contrast, the $Bi_4V_2O_{11}$, compound with $n = 1$ and which was first reported in 1986 by Russian researchers [10], presents 0.5 vacancies in the anionic sublattice, leading to an important ionic conductivity at a relatively low temperature [11]. This phase exists in three polymorphs α, β and γ. The α-$Bi_4V_2O_{11}$ (orthorhombic) exists between the room temperature and 450 °C. The β variety (orthorhombic) is stable between 450 and 580 °C; and beyond this temperature we find the γ polymorph (tetragonal). The γ-$Bi_4V_2O_{11}$ is characterized by a large disorder of oxygen atoms of the $(VO_{3.5})^{2-}$ blocks which is responsible for the high ionic conductivity (0.2 S cm^{-1} at 600 °C [11]) (Table 1).

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Table 1
Values of sintered density, relative density and grain size at different sintering temperatures

x	Sintering temperature (°C)	Density[a] (g/cm^3) (from mass and sizes)	Relative density (%)	Grain size (μm)
0.05	780	6.43 ± 0.05	82.4	6–10
	800	6.55 ± 0.05	84	8–12
	830	6.45 ± 0.05	82.7	16–22
0.10	780	6.47 ± 0.05	82.8	5–8
	800	6.57 ± 0.05	84.2	10–12
	830	6.41 ± 0.05	82.3	15–20
0.15	780	6.44 ± 0.05	82.6	7–10
	800	6.51 ± 0.05	83.7	10–12
	830	6.46 ± 0.05	82.9	15–21

[a] The listed values of density represent average values of density measured on two pellets.

Abraham et al. have succeeded in 1990 to stabilize the γ polymorph by doping $Bi_4V_2O_{11}$ with copper leading to a new series of solid solutions known under the acronym BIMEVOX and formulated $Bi_4V_{2-x}M_xO_{11-\delta}$ [12]. Since then intensive studies of other BIMEVOX materials have been carried out [13–26] and have demonstrated their technological interest as separator of oxygen from air [27] and as cathode in primary lithium batteries: For instance $Bi_4V_2O_{11}$ react with 28 lithium ions per formula and develop a high theoretical specific energy of 840 Wh kg^{-1} [28]. Also, it has been established that the best conductivities is always obtained when 10% of V^{5+} in the native phase, $Bi_4V_2O_{11}$, has been substituted by 10% of the metal independently of its oxidation state and its nature [29]. Some other works have focused on $Bi_4V_{1.8}M_{0,1}M'_{0,1}O_{11-\delta}$ solid solutions (M is a divalent element and M' is tetra or pentavalent cations) with the aim of an enhancement of the ionic conductivity by some "synergic effect" [30–32]. So, we have recently reported detailed study of materials obtained by double substitution of V^{5+} by copper and cobalt in the limit of 10% [32] and we have found that the electrical performances have been improved. However, it is worthwhile to point out that the effect of the double substitution on the electrical properties is diverse. If Vannier et al. have not observed any improvement in the oxide anion conductivity in the case of materials with M and $M' = Cu^{2+}$, Ni^{2+} and Zn^{2+} [30], Paydar, in contrast, has recently reported an increase of the ionic conductivity of the compound with $M = Cu^{2+}$ and $M' = Ti^{4+}$ [31].

Since no particular rule explaining the diverse in the results has been pointed out, we have undertaken the study of doubly substitution of vanadium in $Bi_4V_2O_{11}$ by mixture of two metals $M = Cu^{2+}$ and $M' = Nb^{5+}$ in the limit of 10%. We have chosen the niobium owing to the important conductivity of $Bi_4V_{1.8}Nb_{0.2}O_{11}$ at relatively moderate temperature $\approx 2.5 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at 550 °C, in spite of its orthorhombic symmetry [33].

Hence, the purpose of this paper is to investigate the effect of such double substitution on the physical properties of the prepared ceramics.

2. Experimental

Different compositions of $Bi_4V_{1.8}Cu_{0.2-x}Nb_xO_{11+3x/2}$ solid solutions, $x = 0.05$, 0.1 and 0.15 have been prepared by conventional solid-state reaction between the corresponding reagent grade oxides. The weighted powders were thoroughly homogenized and grinded in agate mortar, then baked in a furnace at 800 °C for 24 h and slowly cooled to room temperature. Several thermal treatments with intermediate regrinding were necessary to obtain pure microcrystalline powders. The powder samples were characterized by X-ray diffraction using an XPERT MPD Philips diffractometer with Cu$K\alpha$ radiation. The patterns were recorded between 10° and 60° (2θ), with a step of 0.02° (2θ) and counting time of 4 s per step.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were carried out between 25 and 800 °C on all the samples using an AT 1500 analyzer at a heating rate of 10 °C min^{-1}. About 20 mg of sample was used for each run.

For the shrinkage studies the powder obtained were milled for 2 h with zirconia ball (20 mm diameter) to reduce the mean particle size. After milling, the powder was sieved with 100 and 25 μm sieves. The fraction below 25 μm was put in the form of cylindrical pellets, about 6 mm diameters and 2 mm thickness, by soft uniaxial hand pressing (0.5 tonne/cm^2). The pellets were sintered, in air, according to the following conditions:

- pellets were introduced into the furnace, the temperature of which has been first stabilized at the sintering temperature T_s;
- the samples were held at T_s for 30 min and quenched from that temperature.

For scanning electron microscopy observations, the faces of the sintered pellets were polished with SiC paper (240–4000 grit) and cleaned with acetone. Microstructural observations were performed on polished samples using a Jeol 5500 scanning electron microscope. Grain boundaries were revealed by thermal etching for 20 min at 50 °C below the sintering temperature. The polished surfaces were coated with a carbon thin film.

The sample conductivity was determined by ac impedance spectroscopy in the frequency range 0.01–1 MHz using a Solartron SI 1260 Impedance Gain Phase Analyser. The amplitude of the ac signal applied across the sample was 50 mV. Measurements were