



Aerosol deposition of (Cu,Ti) substituted bismuth vanadate films



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ABSTRACT

Bismuth vanadate, $\text{Bi}_4\text{V}_2\text{O}_{11}$, and related compounds with various metal (Me) substitutions, $\text{Bi}_4(\text{Me}_x\text{V}_{1-x})_2\text{O}_{11-8x}$, show some of the highest ionic conductivities among the known solid oxide electrolytes. Films of Cu and Ti substituted bismuth vanadate were prepared by an aerosol deposition method, a spray coating process also described as room temperature impact consolidation. Resultant films, several microns in thickness, were dense with good adhesion to the substrate. Scanning electron microscopy and high temperature X-ray diffraction were used to monitor the effects of temperature on the structure and microstructure of the film. The particle size remained nano-scale while microstrain decreased rapidly up to 500 °C, above which coarsening and texturing increased rapidly. Impedance measurements of films deposited on inter-digital electrodes revealed an annealing effect on the ionic conductivity, with the conductivity exceeding that of a screen printed film, and approaching that of bulk ceramic.

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1. Introduction

Technologies using oxygen ion conduction are used in a wide range of applications such as energy conversion and measurement engineering. Many devices like gas sensors, fuel cells and exhaust gas catalysts require fast ion conducting ceramics. Besides the well-established stabilized zirconia system, several other ceramics show suitability as solid oxide electrolytes, e.g. compounds based on LaGaO_3 [1], $\text{La}_2\text{Mo}_2\text{O}_9$ [2], doped ceria [3] and $\text{Bi}_4\text{V}_2\text{O}_{11}$ [4–6].

Compared to stabilized zirconia, bismuth vanadate $\text{Bi}_4\text{V}_2\text{O}_{11}$ (BiVOx) and related compounds with metallic substitutions ($\text{Me} = \text{Cu}^{2+}$, Co^{2+} , Ni^{2+} , Ti^{4+}) $\text{Bi}_4(\text{Me}_x\text{V}_{1-x})_2\text{O}_{11-8x}$ (BiMeVOx) exhibit a higher oxygen ion conductivity especially at moderate temperatures of 500 °C and below [7]. The atomic structure consists of alternating layers of $(\text{BiO}_2)^{2+}$ and $[(\text{V}/\text{Me})\text{O}_{3.5}]^{2-}$ and undergoes a series of transformations (α – β – γ) starting from the room temperature α -phase (orthorhombic) up to high temperature γ -phase (tetragonal symmetry) with increasing temperature [8]. The γ -phase has higher concentration and disorder of mobile oxygen vacancies than the α -phase, yielding a higher ionic conductivity. In order to retain the higher conductivity, a γ -like-phase (γ') can be stabilized to lower temperatures by the addition of the abovementioned metallic substitutions. Oxygen ion conduction takes place along diffusion pathways within the $[(\text{V}/\text{Me})\text{O}_{3.5}]^{2-}$ layer, oriented perpendicular to the c -axis of the tetragonal cell [9]. Double substitution with Cu and Ti, $\text{Bi}_4\text{V}_{1.9}\text{Cu}_{0.05}\text{Ti}_{0.05}\text{O}_{11}$ (BiCuTiVOx), has shown some of the highest conductivities and an improved chemical stability compared to BiVOx and singly substituted compounds [4,10].

Bulk samples of BiMeVOx can be prepared by conventional sintering at temperatures up to 800 °C or by hot-forging [4], which enables high densities and possible texturing of the structure [11]. Films of BiMeVOx have been produced by a few coating techniques like chemical vapor deposition [12], pulsed laser deposition [13] and screen printing [14]. One can imagine that aerosol deposition (AD) might be an ideal technique to fabricate thick film BiMeVOx for applications such as solid oxide fuel cells, where an electrolyte with maximum density is necessary. A spray process such as AD also offers high deposition rates and potential economic benefits.

The “aerosol deposition” (AD) method, alternatively called “Room Temperature Impact Consolidation” (RTIC) is a spray coating method which has been used to build a variety of thick and thin film ceramics [15–17], but until now is not yet used for BiMeVOx . Powder AD is different from other (chemical or liquid) aerosol methods, and offers several advantages over other coating technologies. Ceramic films with a high adhesion to the substrate can be prepared by simply spraying a suitable raw powder at room temperature [16]. Only a rough vacuum in the range of 1 to 10 mbar is necessary. The formation of fully dense ceramic films is possible without additional heat treatment, thereby enabling the deposition on low-melting metals [18,19] or even polymers [20] that would not withstand usual sintering temperatures. Also, the deposition of materials which would decompose, change oxidation state, or react with the substrate during sintering is made possible [21].

A typical AD apparatus consists of an aerosol generation device, a deposition chamber and a vacuum pump [21]. Ceramic powders are kept in a continuously vibrating aerosol chamber. By passing a carrier gas in the bulk powder, a fluidized bed develops and particles are transported, driven by a pressure difference, from the aerosol chamber

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through tubes and a nozzle to the evacuated deposition chamber. The aerosol is then accelerated by the nozzle to velocities above 150 m/s [22] forming an aerosol jet at the nozzle outlet. Powder particles collide with the substrate at high speed resulting in a breakdown of the starting particles to smaller fragments that form the ceramic film. Depending on the material characteristics of both the powder coating and the substrate, only particles with a suitable size will be deposited as a ceramic layer. Though the detailed film formation process has not yet been fully understood, it is suggested that it is associated with the formation of fresh surfaces during cracking of colliding particles [16]. The fresh surface is possibly reactive enough to achieve a chemical bond between the substrate and the particles on one side and then between the particles themselves on the other side. Our objective is to investigate the properties and thermal changes of BiCuTiVOx films deposited by AD.

2. Experimental details

A powder with the composition $\text{Bi}_4(\text{Cu}_{0.05}\text{Ti}_{0.05}\text{V}_{0.9})_2\text{O}_{10.8}$ (BiCuTiVOx) was made using commercially available reagent grade oxides of bismuth, copper, titanium und vanadium, and a conventional mixed oxide route, described in ref [4]. Stoichiometric amounts of raw oxides were mixed and milled for 5 h in a rotary ball mill using zirconia media and de-ionized water as the liquid vehicle. Afterwards the mixture was dried and calcined in air at 630 °C for 12 h and then re-milled for 12 h in water, and dried. In order to further reduce the particle size and enhance the aerosol deposition, powders were again ground for 4 h in a high energy planetary ball mill using cyclohexane as milling fluid. The particle size distribution (measured by Malvern Mastersizer 2000) of the resulting powder is shown in Fig. 1. The powder had a d_{50} value of 2.9 μm .

Prior to deposition, the powder was sieved (mesh size 90 μm) to break down large soft agglomerates which negatively influence the aerosol generation and film building process. The particle size distribution shown in Fig. 1 is still relevant after sieving because all ultrafine powder particles have a diameter smaller than 50 μm and therefore pass the sieve opening. The powder was then dried at 200 °C for 48 h to obtain a free-flowing powder. The AD process was performed using a custom-made AD apparatus already reported in [21]. Suitable spraying parameters were first determined by spraying films on alumina substrates and are summarized in Table 1.

A film with an area of 6 mm $\times$ 5 mm and a thickness of 5 μm was deposited onto a screen printed gold inter-digital electrode (IDE) on an alumina substrate (Ceramtec, Rubalit 708S). The IDE structure consisted of two separated gold electrodes with $n = 15$ fingers on each side. The width of the electrode fingers and the spacing, d , between them is 100 μm with a height of 5 μm . The details of the IDE and its preparation have already been described in [23].

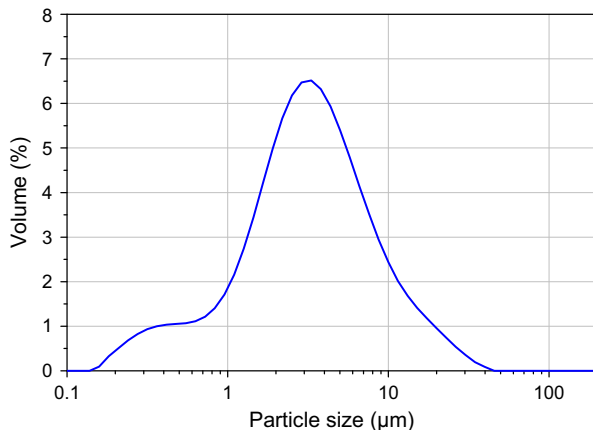


Fig. 1. Particle size distribution of BiCuTiVOx used for AD.

Table 1
Spray parameters of AD BiCuTiVOx films.

Size of nozzle orifice	5 $\times$ 0.5 mm ²
Nitrogen gas flow	4–8 l/min
Scanning speed	0.5 mm/s
Spraying distance	3 mm
Shaking frequency of aerosol container	400 rpm
Pressure in aerosol chamber	20–40 kPa
Pressure in deposition chamber	0.1–1 kPa

For comparison, screen printed films were also made. A thick-film paste incorporating BiCuTiVOx powder was prepared using terpeneol and ethyl cellulose as vehicle. Films were screen printed on identical IDE-structures (6 μm), alumina (5 μm) and silicon (5 μm) and afterwards sintered at 750 °C in air. Film thickness and surface roughness R_a were measured by a Mahr Perthometer PGK/S2 based on the tactile stylus method. Conductivity measurements were performed in a fused-quartz tube furnace upon heating between 200 and 500 °C with 50 °C steps in an atmosphere of 10% oxygen. The furnace and sample were heated at a rate of 5 K/min and allowed to equilibrate for 15 min before measurement. A precision impedance analyzer (Novocontrol) was used to measure impedance characteristics in a frequency range from 10 MHz to 1 Hz at 50 mV rms amplitude of the ac signal. Measured spectra were fitted to a parallel RC element to determine the resistance R . The conductivity was then calculated in accordance with [24] by measured resistances R , film thickness t , and the IDE-geometry (finger length $l = 4.5$ mm, finger width $w = 100$ μm , spacing between fingers $d = 100$ μm and number of fingers $n = 15$):

$$\sigma = \frac{d}{R \cdot [(2n-1) \cdot l \cdot t + 2n \cdot w \cdot t]} \quad (1)$$

The influence of a post-deposition heat treatment on the structure and microstructure of BiCuTiVOx AD films was investigated. Films with 3–4 μm thickness deposited on alumina were annealed at temperatures in the range of 200 to 800 °C and then examined by scanning electron microscopy (SEM) using a Zeiss Leo Gemini 1530 (operating voltage 20 kV). Films of slightly higher thickness (5 μm) were deposited on silicon substrates (Crystec, boron doped, orientation (100), 525 μm thickness) for X-ray diffraction (XRD) analysis using a PANalytical XPert Pro diffractometer with a hot stage. Nickel-filtered $\text{Cu K}\alpha$ radiation was used as the X-ray source. The scanning was done in the 2θ range of 10° to 65° with a step size of 0.017°.

Silicon was chosen as substrate material due to its sharp, well defined and mostly non-overlapping peaks, enabling easy differentiation between film and substrate. XRD patterns were collected at room temperature and at 50 °C intervals between 300 and 800 °C, with a dwell time of 20 min at each step to allow the sample to thermally equilibrate prior to measurement. *X'Pert HighScore Plus* software, with included algorithms for Rietveld-refinement, was used for structure verification and indexing to the γ -phase (tetragonal space group $I4/mmm$), according to the published powder diffraction file for BiCuVOx [25] based on structural work by Yaremchenko [26]. Crystallite size and microstrain were calculated using the software based on the Rietveld-refinement with pseudo-Voigt fitting function. Film texture was calculated using the Lotgering orientation factor [27], f

$$f = \frac{p - p_0}{1 - p_0} \quad (2)$$

$$p = \frac{\sum_l I(00l)}{\sum_{hkl} I(hkl)} \quad (3)$$

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