POTENTIAL BARRIER BEHAVIOR IN BICUVOX MATERIALS

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The BiMeVOx materials appear being high attractive for applications at low temperatures when the ionic conductivity is the determining parameter. The occurrence of many types substitution was confirmed for numerous Me ions, but the greatest interest have been focused on the BiCuVOx materials. The objective of this work was to image the potential barriers in BiCuVOx. The sample was sintered for 4 hours at 750°C and the results show that the high density compound can be obtained. Simultaneously, topography and electric force microscopy (EFM) images are viewed side-by-side in the Nanoscope IIIa SPM controller (Digital Instruments/Veeco Metrology, Inc., Santa Barbara, CA). EFM experiments were performed and the results show the maps of the electric field distribution on the surface of BiCuVOx. The formation of potential barrier was observed and the width and intensity were measured.

Keywords: BiCuVOx, EFM, potential barrier

INTRODUCTION

The solid electrolytes are materials that block the passage of liquids and gases, but allow the transport of ions through the network when there is a tendency to diffusion. The conductor’s oxygen ions are extensively studied and used for a variety of applications, such as oxygen sensors and fuel cells.

Solid electrolytes, also known as fast ionic conductors are a class of materials with significantly higher low-temperature conductivity than would be expected from a simple statistical assumption regarding the number of vacancies. The measured oxide-ion conductivities were indeed quite high, and the transport number near unity [2-4]. Abraham’s [5] report spurred a flurry of other papers reporting various partial substitutions of other elements for the Bi, V, or both metals in the structure, and the resulting modifications to the ionic conductivity. The high oxide ion conductivity reported for the BiMeVOx family is believed to be due to the disorder of the oxygen vacancies that are associated with the vanadium atoms in the perovskitic layer.

Mairesse [6] has summarized results for the substitutions of various metal cations onto the vanadium site.

This study was based in ceramics solid electrolytes BiMeVOX (Bi=bismuth, V=vanadium, OX=oxygen and, Me=Cu) for conducting oxygen ions, using the method of fusion of oxides as technique of synthesis of the main phase whose compositions are based on the use of Cu^{2+} metal ions. BiCuVOX has potential applications as a fast- ion conducting component in solid oxide fuel cells, oxygen gas sensors and electrochemical pumps for oxygen separation. This material is derived from $Bi_4V_2O_{11}$ whereby vanadium is partially substituted by copper. The gamma phase of $Bi_4V_2O_{11}$ is the ionic conducting phase. The gamma phase is unstable, but can be stabilized by partial substitution with copper or cobalt [1].

MATERIALS AND METHODS

Materials

The materials used as basic reagents in the formulation of BiCuVOX sample were produced by Aldrich, and follow: Bismuth oxide (Bi_2O_3), vanadium oxide (V_2O_5), copper oxide [$Cu\ (NO_3)_2$], titanium oxide (TiO_2).

Sample Preparation

The powders of crystalline oxides were be prepared with compositions based on the addition of Cu^{2+} at BiMeVOX the main stage by fusion of oxides technique. These powders are milling in alcohol medium (in mill of balls of zirconia). The samples were compressed in the cylindrical pellets by isostatic pressing with a size of approximately 10 mm in diameter and 3 mm thick. Before, the sample were submitted to thermal treatment carried out in electric furnace in air, for times, temperatures and heating rates appropriated

Electrostatic Force Microscopy (EFM)

The potential barrier analysis was performed in a atomic force microscopy Nanoscope IIIA (Digital Instruments) operating in a electric force microscopy mode (EFM) that was equipped with an extender electronic module (Veeco Instruments, Santa Barbara, CA). Topographical measurements and electrical data were obtained by the two-pass technique (Lift Mode). In this configuration, during the first pass, the probe (operating in TappingMode) scans a topographical line. In the second scan, the cantilever is lifted to a predefined distance (75 nm) in order to minimize the effect of the van der Waals forces, during which it detects variations in the electrical force gradient over the same line and the influence of surface topography is ruled out 25-28. A NSC15 tip (MikroMasch) was used in all the experiments. Electrostatic force gradient images were obtained by monitoring the shifts in phase and frequency between the oscillations of the biased. The cantilever and those of the piezoelectric driver as a function of bias voltages applied to the cantilever. The initial EFM imaging conditions were: interleave frequency drive, 25 Hz; integral gain, 0.35; proportional gain, 2.5. The images of surface potential and barrier layer were obtained by applying 4, 8 and 12 V in situ to the sample. Imaging was carried out at room temperature.

RESULTS AND DISCUSSION

The microstructural and electrical properties analysis of BuCuVOX sample was analyzed by scanning probe microscopy (SPM): AFM combined with EFM. The results were analyzed and interpreted using the Software DI which is specific to specific analysis of images of this technique.

Figure 1 show images obtained via AFM/EFM to BiCuVOX when subjected to different voltages. Figs. 1(a) provide topographic informations. The microstructure shows no pores. The grains appear to be homogeneously which indicate that the densification occurred completely.

The EFM results has been presented in Fig. 1 (b, c, d, e) with application of external voltage from 4 volts to 12 volts, showing details about the variations in the electric field gradient. The results presented in EFM images shows that the increase of the applied voltage leads to an increase in concentration of negative loads in grain behavior evidencing the presence of effective potential barrier (or attractive).

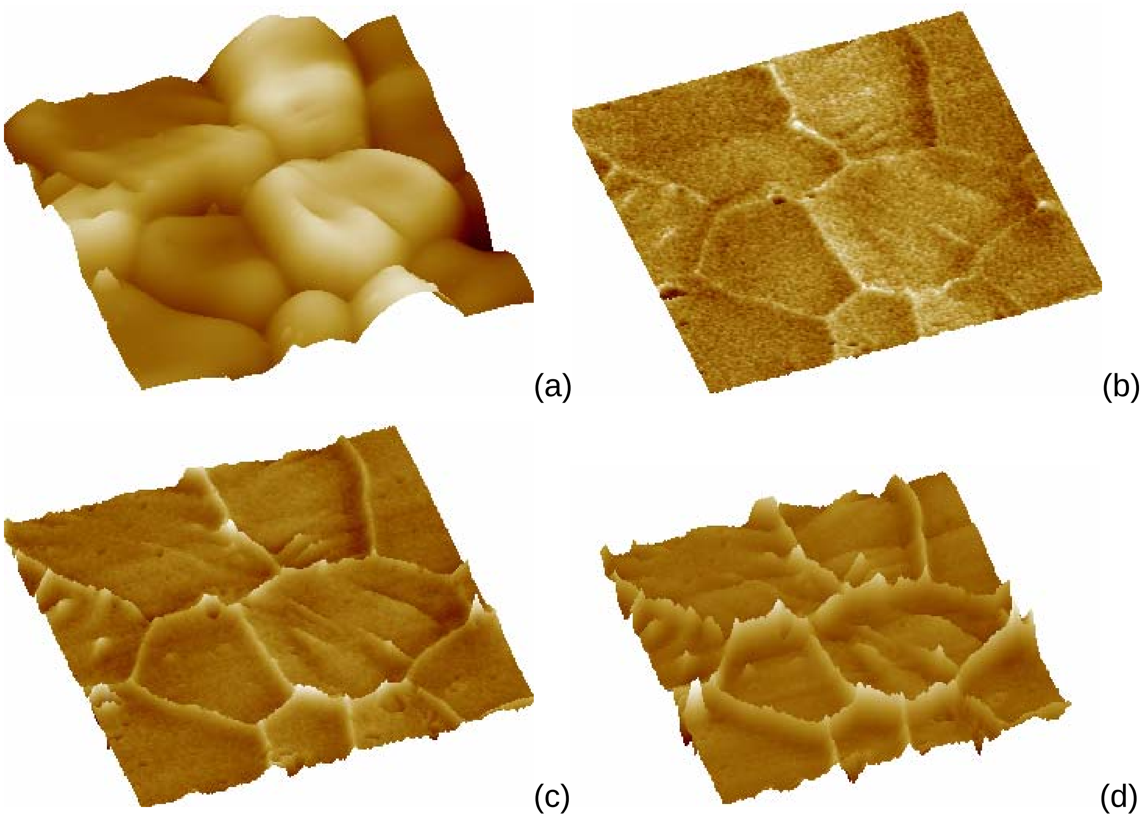

Figure 1 – Analysis of BiCuVOX by AFM/EFM: (a) 3D topography image $(10\times10\times1.2)\mu m$; 3D profiles EFM with application of external voltage $(10\times10)\mu m$: (b) 4 volts (c) 8 volts, (d) 12 volts

The EFM images registers of potential barriers found in the grain contours. The paths of electrical current are those of less resistance, or be, routes with less borders (or larger grains) and those with smaller grain boundary barrier. If the grain size is uniform then, more electric current pass through of many parallel paths.

The origin of these barriers is interface charge stemming from lattice mismatch, defects and dopants at the grain boundary. The interface charge changes the Fermi level in the vicinity of the grain boundary, with band bending as a result. The electronic charges stored in an interface represent a repulsive potential for the majority carriers – the electrons in the case of an n-doped semiconductor – across the interface.

CONCLUSION

The use of atomic force microscopy techniques, electric force microscopy, shows a powerful tool in analyzing phenomena associated to grain boundaries regions. The potential barriers formed at grain boundaries due segregation of dopants in these regions, as stated in the literature, could be imaged in situ. The potential barriers, due electrical forces developed at interfaces, detected by EFM, are in agreement with theoretical models proposed in the literature.

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