DEPENDENCE OF SENSITIVITY ON GRANULOMETRY IN CONDUCTIMETRIC γ´-Bi_2MoO_6 SENSORS

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Abstract

The sensitivity to ethanol, in O_2/N_2 carrier gas, of γ´-Bi_2MoO_6 sintered pellets of 10 μm average grain size, is compared with that of thin films, obtained by thermal oxidation of magnetron sputtered, stoichiometrically layered Bi-Mo deposits, with an average grain size of 0.5 μm. Pellet response to a 1.3 % w/w ethanol stimulus, at 500 °C, is 47 %, quantitatively accounted by an increase in ionic conductivity, as evaluated by impedance spectroscopy. This response is totally absent in thin films, under the same conditions, due the increase in electronic and surface conductions.

Resumen

La sensibilidad a etanol en pastillas sinterizadas de la fase γ´-Bi_2MoO_6, con un tamaño de grano de 10μm, se compara con la de películas delgadas multicapa, obtenidas por deposición por plasma magnéticamente confinado de Bi-Mo y oxidadas térmicamente, con un tamaño de grano promedio de 0.5 μm. Para una concentración de etanol del 1.3 % m/m, en el caso de pastillas, el cambio resistivo es de 47 %, a 500 °C, atribuible a un aumento en la conductividad iónica, como demuestra la espectroscopía de impedancia. Las películas delgadas carecen de sensibilidad en las mismas condiciones, debido al aumento de conducción electrónica y superficial.

Introduction

The use of fast oxygen ionic conductors in electrochemical membranes, suitable for potentiometric measurement, is widespread in gaseous metrology, whereas conductimetric applications are not as frequent.

Solid ionic oxygen electrolytes can incorporate O_2 from the gaseous phase and transport it via point defect mediated mechanisms, conditioned by bulk ionic conductivity, electronic conductivity and the rate of gas-solid oxygen exchange. Ionic conductivity

dominance usually requires operating temperatures in excess of 600 °C, which current research attempts to reduce.

Binary Mo Bi oxides are well known as selective alkene oxidation catalysts [1]. The crystalline structure of γ'-Bi_2MoO_6 (or γ(H)) [2-4] allows O^{2-} intracrystalline diffusivity mediated by high vacancy [5], leading to high oxygen ion conductivity at temperatures < 600 °C [6, 7]. Its electrical conductivity increases the concentration of oxygen vacancies, which has motivated its application as a conductimetric sensor [8, 9].

The sensing mechanism is intimately related to the catalytic properties of the γ´ phase, involving redox reactions between gaseous O_2 and lattice O^{2-}, similar to the Mars van Krevelen [10] mechanism. This close parallel suggests that a minimum grain size contributes to enhance sensitivity.

In this study, the sensitivity to ethanol, with O_2/N_2 as carrier gas, of γ´-Bi_2MoO_6 sintered pellets of 10 μm average grain size is compared with that of thin films, obtained by thermal oxidation of magnetron sputtered, stoichiometrically layered Bi-Mo deposits, which yield an average grain size of 0.5 μm.

Experimental

1.- Sample preparation

Sintered pellets of the γ´-Bi_2MoO_6 phase were prepared by solid state reaction of a stoichiometric mixture of its component oxides, in air, at 900 ºC, for 6 hrs. The resulting product was the high temperature γ´-Bi_2MoO_6 phase, which is known to be formed irreversibly at 660-690 °C, from an equimolar mixture of Bi_2O_3 and MoO_3 [2, 11]. Complete reaction was confirmed by XRD (Fig. 1) and the (Fig. 2) average grain size was 10 μm as determined by SEM.

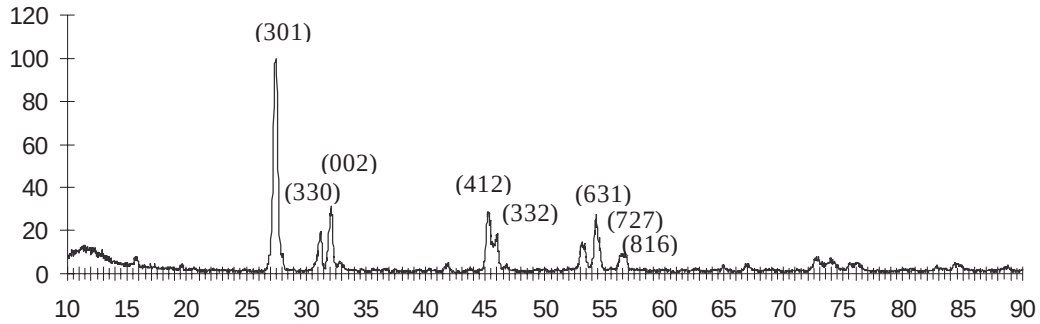

***Figure 1**.- Cu K_α XRD spectrum of γ´-Bi_2MoO_6 pellets.*

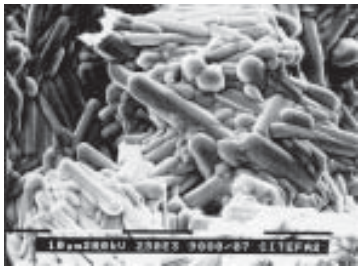

***Figure 2**.- SEM micrograph of γ´-Bi_2MoO_6 pellet sintered at 900°C in air*

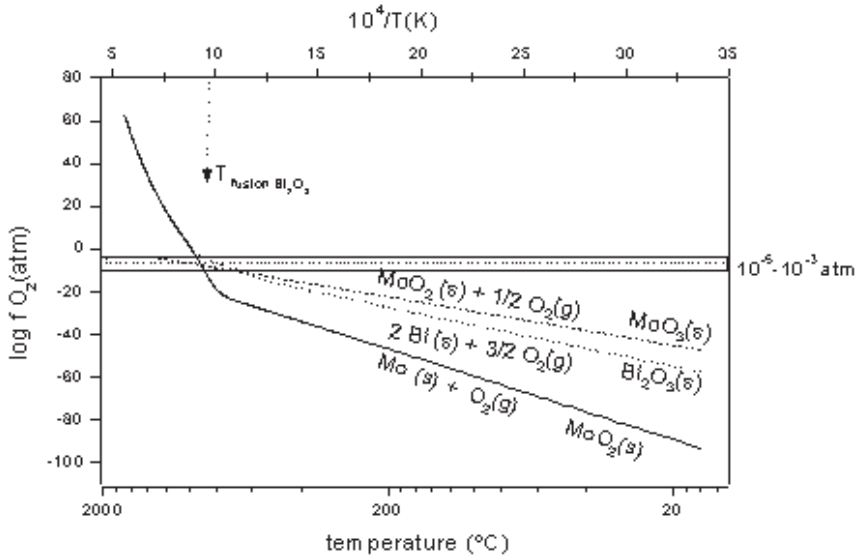

Figure 3.- *Phase diagram of Bi-Mo oxides*

The phase diagram (Fig. 3) demonstrates that the thermodynamic stability of the constituent oxides precludes the use of vacuum thermal evaporation methods, if the desired metal-oxygen stoichiometry is to be preserved, because heating would induce oxide decomposition by reduction to metals.

Mo-Bi bimetallic thin films, layered in stoichiometric proportion to a thickness of 100 nm, were obtained by sequential D.C. magnetron co-sputtering with fully decoupled parallel plasmas. Under 10^{-3} mbar of argon, with independent current control of each cathode, on AlSiMag® Technical Ceramics Inc. substrates, mounted on a rotating stage. The sputtered films were subsequently thermally oxidized, at 500 °C, in air. Thin film structure was preserved, without loss of adhesion, and the phase was confirmed by XRD (Fig. 4), with a SEM (Fig. 5) determined average grain size of 0.5 μm.

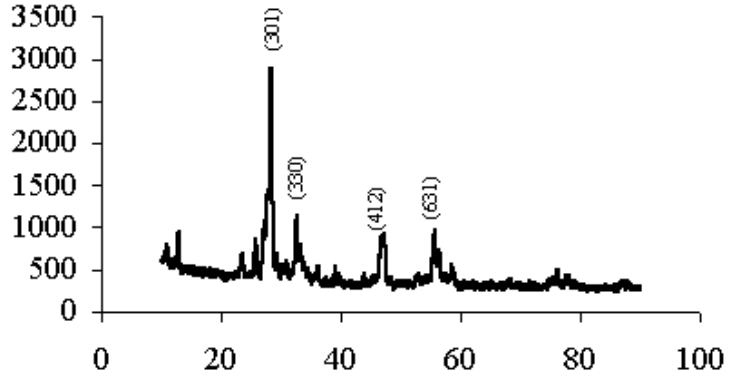

Figure 4.- *XRD spectrum of Bi_2MoO_6 thin film annealed at 500 °C*

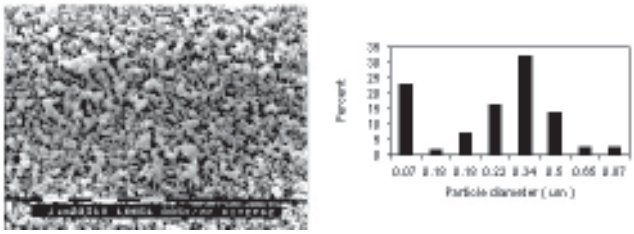

Figure 5.- *SEM micrograph and grain size distribution of Bi_2MoO_6 thin film annealed at 500 °C*

2.- Conductivity measurements

Gold electrodes were magnetron sputtered to a thickness of 100 nm on both faces of the pellets, which were mounted on a spring loaded ceramic fixture, in a cylindrical sillimanite reactor. The support harness was fitted with Pt conductors, in pseudo 4-probe configuration and a Platinel II thermocouple.

A.C. measurements (50 mV rms, at 10 Hz) were obtained with an EG&G Signal Recovery DSP 7265 lock-in amplifier and a custom I/V preamplifier (10^4 V/A), in N_2/O_2 atmospheres, regulated by MKS 1179 A mass flow controllers, at 500 °C. A constant flow of 100 cm^3/min was used, in which ethanol saturated N_2 was mixed with a fixed concentration of 1.3 % w/w.

Results and Discussion

The γ´-Bi_2MoO_6 pellet response to a 1.3% w/w ethanol stimulus, at 500 °C (Fig. 6), is 47 % quantitatively matching the ionic conductivity increase, as evaluated by impedance spectroscopy (Fig. 7). Conductive sensitivity to ethanol is inversely proportional to oxygen partial pressure in the carrier gas (Fig. 8), consistently with the increase of concentration of lattice oxygen vacancies in the oxide phase, under reducing conditions. In all instances, the response to chemical stimulus is stable and a stationary regime attained. For the transient mode, the response time to 80 % of the stationary limit is on average, 200 s.

The response to ethanol is totally absent in thin films monitored under identical conditions (Fig. 9).

The conductimetric sensing mechanism of Bi_2MoO_6 devices is closely related to its well known catalytic properties for selective oxidation reactions. Since the gas-solid interaction required by either application is enhanced by high specific area textures, small grain size is generally favoured. However, conductivity measurements in these mixed ionic-electronic conductors demonstrate the existence of coupled transport regimes, mediated by surface and bulk migration paths, which condition sensitivity.

A drastic difference is observed in the sensitivity of sintered pellets and thermally oxidized thin films, which is attributed to differences in the prevailing conduction mechanism. In coarse grained sintered samples, ionic intracrystalline conduction is dominant, whereas prevailing grain boundary conduction inhibits response in thin films.

Increased sensitivity at coarser grain size is attained at the expense of response time, which suggests that the optimum device configuration requires thick film technology. Preliminary results of ongoing studies confirm this hypothesis

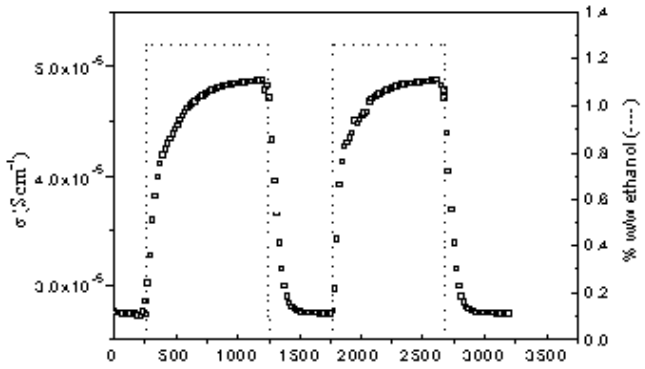

***Figure 6**.- Electrical conductivity dependence of γ´-Bi_2MoO_6 at 500 °C in ethanol.*

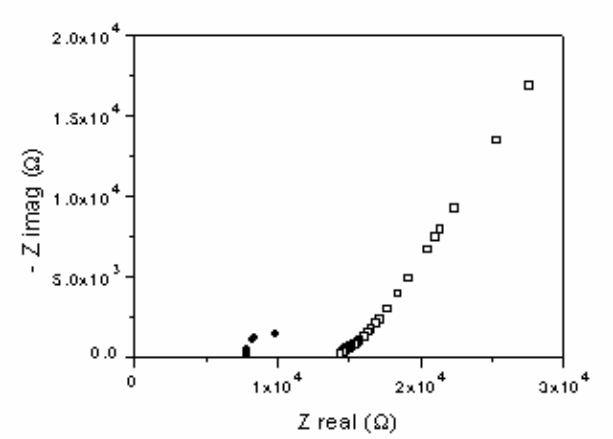

***Figure 7.**- Impedance spectroscopy of γ´-Bi_2MoO_6 at 500 °C before and after exposure to ethanol, (□) in N_2 atmosphere , (●) 1.3 % by weight ethanol in N_2.*

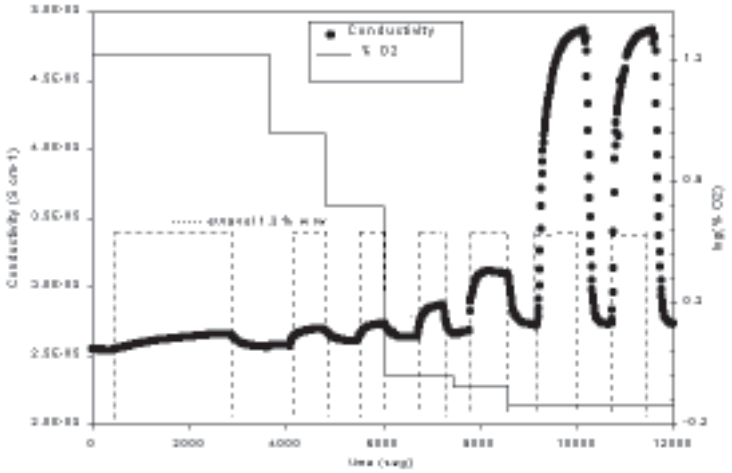

***Figura 8**.- γ´-Bi_2MoO_6 conductimetric response to 1.3 % w/w ethanol (dashed line) stimulus, in decreasing O_2 in N_2 (full line) carrier gas composition.*

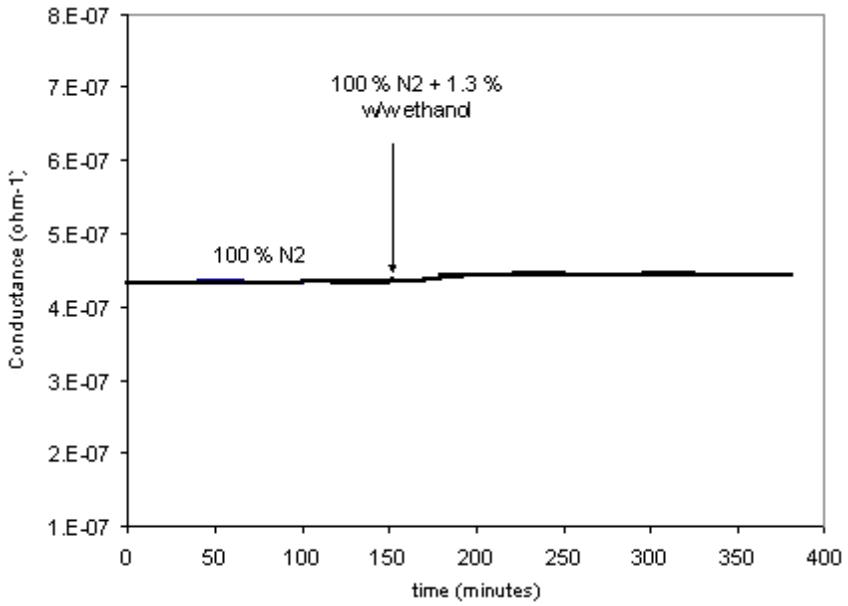

Figure 9.- *γ-Bi_2MoO_6 thin films conductimetric response to ethanol stimulus.*

Conclusions

In γ´-Bi_2MoO_6 conductimetric sensors, ethanol sensitivity is dependent on grain size. 10 μm-grained pellet response, to a 1.3 % w/w ethanol stimulus, at 500 °C, is 47 % quantitatively accounted by an increase in ionic conductivity, whereas in 0.5 μm-grain sized thin films, this response is totally absent, under identical conditions, due to enhanced electronic and surface conductions.

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