ELSEVIER

Oxygen partial pressure dependence of electrical conductivity in γ′-Bi₂MoO₆

C.M.C. Vera[a],*, R. Aragón[a,b]

[a]*Laboratorio de Películas Delgadas, Facultad de Ingeniería, Universidad de Buenos Aires, Paseo Colón 850, (1063) Buenos Aires, Argentina*
[b]*CINSO, CONICET, CITEFA, Lasalle 4397, Villa Martelli, Buenos Aires, Argentina*

Abstract

The electrical conductivity of γ′-Bi₂MoO₆ was surveyed between 450 and 750 °C as a function of oxygen partial pressure, in the range 0.01–1 atm. A $-\frac{1}{6}$ power law dependence, consistent with a Frenkel defect model of doubly ionized oxygen vacancies and interstitials, is evidence for an n-type semiconductive component, with an optical band gap of 2.9 eV. The absence of this dependence is used to map the onset of dominant ionic conduction.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

The orthorhombic oxide γ-Bi₂MoO₆ is constituted by layers of $[MO_4^{2-}]_n$ and $[Bi_2O_2]_n^{2+}$ linked by O^{2-}. Three polymorphs have been described: γ below 570 °C, γ″ between 604 and 640 °C, and the high temperature γ′ phase into which they transform irreversibly. In the latter, the $[Bi_2O_2]_n^{2+}$ layers reorder conforming rows of channels in a Latin cross configuration, which make fast oxygen transport possible [1,2].

The high mobility of oxygen in the layered γ′-Bi₂MoO₆ structure mediates its catalytic properties in selective oxidation of organic reagents. Although electrical transport in this phase is generally acknowledged to be a thermally promoted process, considerable disagreement persists on the relevant conduction mechanism, which has been alternatively attributed to n-type semiconduction [3], fast ionic [4] and mixed [5–7] ionic–electronic conduction.

Impedance spectroscopy studies [8] have shown that electrical transport in typical ceramic samples includes, in addition to ionic and electronic components, grain boundary as well as intracrystalline contributions, which can obscure the dependence of electrical conductivity on partial pressure of oxygen, relevant to the underlying point defect structure.

2. Model conduction in MO

The derivation of the pertinent phenomenological relations can be summarized briefly, invoking a simple undoped semiconducting metal monoxide MO, as a model for the pseudobinary approximation, with a Frenkel point defect structure symbolized by the Kröger–Vink [9] notation:

O_O : lattice oxygen
M_M: lattice metal
O_i: interstitial oxygen
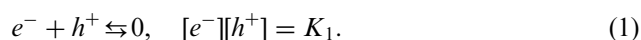M_i: interstitial metal
V_O: oxygen vacancy
V_M: metal vacancy
V_i: interstitial vacancy
$[a]$: concentration of species a

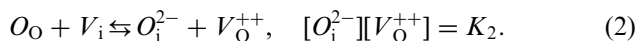The three pertinent reactions [10,11] and their associated equilibrium expressions are:
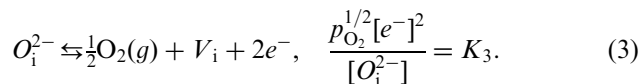
(1) Electron–hole annihilation

$$e^- + h^+ \leftrightarrows 0, \quad [e^-][h^+] = K_1. \tag{1}$$

*Corresponding author.
E-mail address:* cvera@fi.uba.ar (C.M.C. Vera).

(2) Oxygen Frenkel disorder

$$O_O + V_i \leftrightarrows O_i^{2-} + V_O^{++}, \quad [O_i^{2-}][V_O^{++}] = K_2. \tag{2}$$

(3) Addition or removal of oxygen by interaction with the gas phase

$$O_i^{2-} \leftrightarrows \tfrac{1}{2}O_2(g) + V_i + 2e^-, \quad \frac{p_{O_2}^{1/2}[e^-]^2}{[O_i^{2-}]} = K_3. \tag{3}$$

Furthermore, preservation of electroneutrality requires that:

$$[e^-] + 2[O_i^{2-}] = [h^+] + 2[V_O^{++}]. \tag{4}$$

This set of equations admits simple solutions, whenever one species is dominant, which results in four generally recognized limiting cases, namely:

I If ionic defect concentrations are negligible, the concentration of holes is equal to that of electrons, yielding intrinsic semiconductor behavior.

II If electronic carrier concentrations are negligible and the partial pressure of oxygen corresponds to the equilibrium value for the stoichiometric phase, Eq. (4) requires $[O_i^{2-}] = [V_O^{++}]$, corresponding to intrinsic ionic conduction, which is invariant with changes in partial pressure of oxygen.

III In the immediate neighborhood of the stoichiometric composition, consistently with low overall electronic carrier concentrations, their relative changes, induced by reactions 1 and 3, are much larger than those corresponding to ionic defects. Consequently, $[O_i^{2-}]$ and $[V_O^{++}]$ may be presumed constant, yielding the approximation:

$$p_{O_2}^{1/2}[e^-]^2 = K_3[O_i^{2-}], \tag{5}$$

hence,

$$[e^-] = K_3' p_{O_2}^{-1/4} \tag{6}$$

and

$$[h^+] = K_3'' p_{O_2}^{1/4}, \tag{7}$$

where $K_3' = (K_3[O_i^{2-}])^{1/2}$ and $K_3'' = (K_1^2/K_3[O_i^{2-}])^{1/2}$.

IV If the imposed partial pressure of oxygen is significantly lower or higher, than the intrinsic equilibrium value for the stoichiometric oxide, the composition of the solid phase must be alternatively represented by $MO_{1-\delta}$ or $MO_{1+\delta}$, respectively, and the previous approximations are no longer valid, instead it is recognized that:

(a) Far below the intrinsic oxygen partial pressure for the stoichiometric oxide, reaction (3) is favored, which yields high $[e^-]$ and low $[h^+]$. Preservation of electroneutrality requires diminished $[O_i^{2-}]$

and increased $[V_O^{++}]$, consistent with the approximation:

$$[e^-] = 2[V_O^{++}]. \tag{8}$$

Substitution in (2) and (3) yields

$$[e^-] = K_3^* p_{O_2}^{-1/6}, \tag{9}$$

where $K_3^* = (2K_2K_3)^{1/3}$.

Far above the intrinsic oxygen partial pressure for the stoichiometric oxide, the reverse holds true, namely low $[e^-]$ and high $[h^+]$. Hence $[O_i^{2-}]$ must increase, whereas $[V_O^{++}]$ decreases, and charge balance requires:

$$[h^+] = 2[O_i^{2-}] \tag{10}$$

and substitution in (1) and (3) yields

$$[h^+] = K_3^{**} p_{O_2}^{1/6}, \tag{11}$$

where $K_3^{**} = (2K_1^2/K_3)^{1/3}$.

Alternatives (a) and (b) correspond to mixed ionic–electronic conduction.

3. Mixed ionic–electronic conduction in γ'-Bi$_2$MoO$_6$

Evidence for electronic semiconducting properties can be readily obtained from diffuse optical scattering [12–14] experiments. The spectrum of a sintered pellet (Fig. 1) between 200 and 850 nm, obtained with a Shimadzu Model UV-2401 PC spectrometer, fitted with an integrating sphere, referred to BaSO$_4$ as 100% reflectance standard, displays a characteristic absorption edge around 450 nm, which corresponds to a band gap (E_g) of 2.9 eV, once the linear part of the corresponding Kubelka Munk remission function (inset Fig. 1) is extrapolated. The power law dependence of the absorption coefficient (α) on incident radiation energy (hv), $\alpha = (hv - E_g)^\gamma$, closely fits an exponent $\gamma = \tfrac{1}{2}$, consistent with a direct gap semiconductor [12].
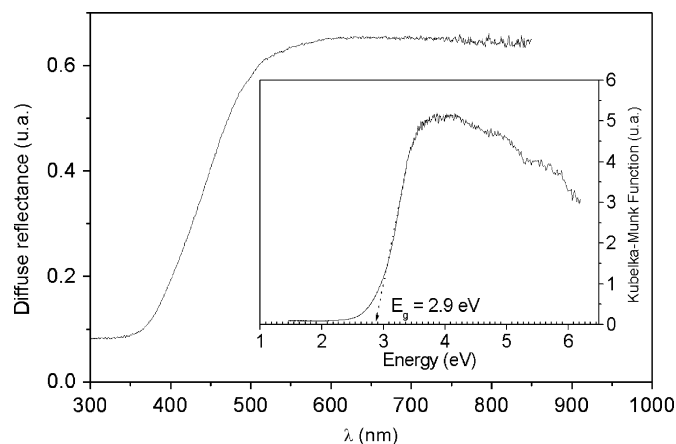

Fig. 1. Diffuse reflectance spectrum of a sintered γ'-Bi$_2$MoO$_6$ pellet, inset: extrapolation to the abscissa of the Kubelka–Munk functional dependence on incident illumination energy yields the semiconductor energy gap.