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OXYGEN DIFFUSION MECHANISMS IN TWO SERIES OF OXIDE ION CONDUCTORS: BIMEVOX AND BROWNMILLERITE MATERIALS

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ABSTRACT

The BIMEVOX and Brownmillerite materials have as common point a layered structure with intrinsic oxygen vacancies. These defects confer to these compounds high oxide ion conduction.

The BIMEVOX were evidenced by members of our group at the end of the eighties. They derive from the parent compound $\text{Bi}_4\text{V}_2\text{O}_{11}$ and were obtained by partial substitution for vanadium with a metal. They are still considered as the best oxide ion conductors at moderate temperature, 400-700°C, but suffer of a lack of stability under reducing conditions.

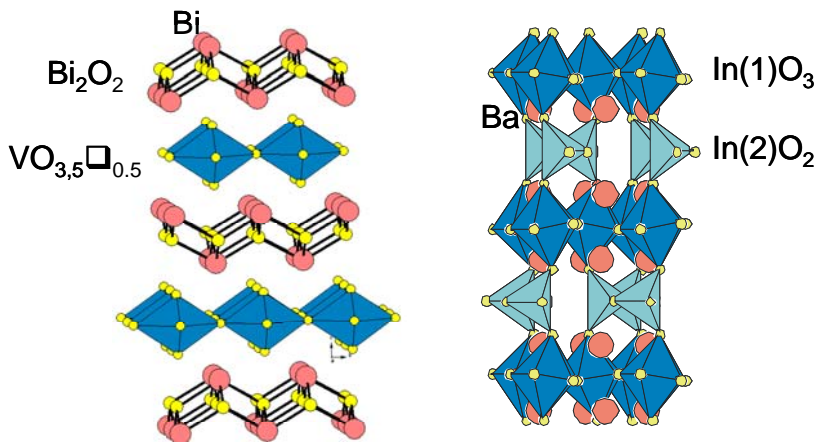
During the same period, Goodenough evidenced high oxide conduction in the Brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$, above 925°C. In order to stabilize this property at lower temperature, numerous partial substitutions were performed on either the Ba or the In site. Our group considered the partial substitution for indium with cations such as Sn, V, Ta, Nb, Mo and W. Solid solutions were obtained for all the dopants. By combining various techniques, among which atomistic simulation, X-ray diffraction, neutron diffraction, impedance spectroscopy, $^{18}\text{O}/^{16}\text{O}$ isotope exchange, the transport of oxygen in these two families of materials was characterized from the atomic scale to the macroscopic scale.

INTRODUCTION

Although discovered since more than one century, the stabilized zirconia remains the more developed material for applications such as Solid Oxide Fuel Cells, sensors or membranes for gas separation. Its properties are due to its cubic structure, similar to that of the fluorite, with extrinsic vacancies.

With a similar structure, the bismuth oxide, Bi_2O_3 , in its high temperature form, δ , can be considered as the best oxide conductor with a conductivity of $1\text{S}\cdot\text{cm}^{-1}$ at 800°C. Despite excellent properties this oxide could not be developed. The δ form is unfortunately stable only on a very narrow domain in temperature, limited by the melting of the oxide to 830°C and by a phase transition at 730°C which is accompanied with strong mechanical strains which make impossible the sintering of this oxide. Under the impulse of Jean-Claude Boivin, the team of Solid State Chemistry at the UCCS devoted a big part of its research to the stabilization of the excellent properties of this oxide at lower temperature¹. The BIMEVOX family was evidenced at the end of the eighties². It derived from the parent compound $\text{Bi}_4\text{V}_2\text{O}_{11}$ and is obtained by partial substitution for vanadium with a metal to allow the stabilization, at room temperature, of the high temperature form, γ , which exhibits high oxide ion conduction above 570°C³. From the structural point of view, most of oxide ion conducting ceramics (except apatites) derive from the fluorite or from the perovskite and the average structure of the BIMEVOX can be described as

an intergrowth of these two structural types. It is built upon Bi_2O_2 layers of the fluorite type spaced with $\text{V}(\text{Me})\text{O}_{3.5}\square_{0.5}$ slabs of the perovskite type which exhibit intrinsic oxygen vacancies. It is the presence of these vacancies and the stereoactivity of the bismuth lone pair which explains the excellent properties of these materials.



In 1990, Goodenough evidenced excellent properties of conduction for the Brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$, above 925°C ^{4,5}. Like BIMEVOX, $\text{Ba}_2\text{In}_2\text{O}_5$ exhibits, at room temperature, a two-dimensional structure. This structure derives from the perovskite and can be described like the intergrowth of layers of octahedrons, $[\text{InO}_3]$, and tetrahedrons, $[\text{InO}_2]$, the barium atoms being located in the sites between these layers. When the temperature increases, the oxygen vacancies located in the tetrahedral layers at room temperature, disorder and the material becomes an oxide ion conductor. Many studies were also carried out to stabilize the high temperatures forms of the Brownmillerite at lower temperature⁵⁻¹⁶. Our team considered the partial substitution for indium with elements of valence higher than three in order to introduce additional oxide ions in the structure¹⁷. Tin, vanadium, molybdenum and tungsten were studied. Solid solutions were obtained in all cases and led to the stabilization at lower temperature of the required forms. By combining various techniques, among which, atomistic simulation, X-ray diffraction, neutron diffraction, impedance spectroscopy, $^{18}\text{O}/^{16}\text{O}$ isotope exchange, the oxygen transport in these two families of materials was characterized from the atomic scale to the macroscopic scale.

OXYGEN TRANSPORT AT THE ATOMIC SCALE

Simulation techniques are based upon energy minimization procedures. Thanks to the description of interatomic potentials, energetics of extrinsic defects and of various mechanisms or pathways for oxygen migration can be explored. The software developed by Gale¹⁸ was used for these calculations. The structure of $\text{Bi}_4\text{V}_2\text{O}_{11}$, with intrinsic oxygen vacancies, being too complicated to simulate and having no model of potential for vanadium, calculations were carried out on a compound of structure close to that of the BIMEVOX: Bi_2WO_6 ¹⁹. Bi_2WO_6 exhibits the same structure as BIMEVOX but without oxygen vacancy. Its electrical properties, initially very weak, were strongly improved when tungsten was partially substituted by tantalum

or niobium²⁰. They were measured by impedance spectroscopy and are compared to those of $\text{Bi}_4\text{V}_2\text{O}_{11}$ and $\text{Ba}_2\text{In}_2\text{O}_5$ in the following figure.

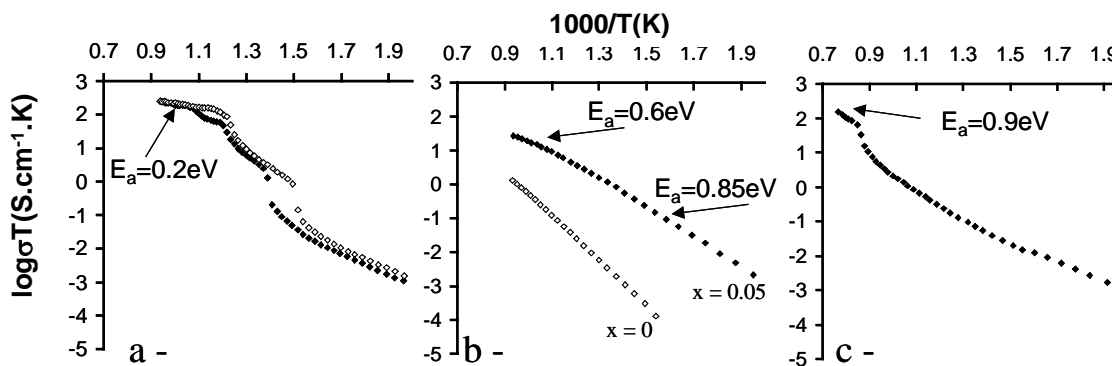


Figure 2. Arrhenius plot of the conductivity of
a) $\text{Bi}_4\text{V}_2\text{O}_{11}$ b) Bi_2WO_6 and $\text{Bi}_2\text{W}_{0.95}\text{Ta}_{0.05}\text{O}_{5.975}$ and c) $\text{Ba}_2\text{In}_2\text{O}_5$

An activation energy of 0.9 eV was observed for the high temperature domain of $\text{Ba}_2\text{In}_2\text{O}_5$, it was only 0.2 eV for the $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ form. For bismuth tungsten oxide partially substituted with 5% of tantalum, two domains were observed on the Arrhenius plot, with an energy of activation of 0.6 eV at high temperature and 0.85 eV below 500°C. To understand the oxygen diffusion mechanisms at the atomic scale, several types of defects were considered in the structures of $\text{Ba}_2\text{In}_2\text{O}_5$ and Bi_2WO_6 . In case of the Brownmillerite, the most favorable defect was the formation of an oxygen vacancy in the octahedral layers associated to an interstitial oxide in the tetrahedral layers. A defect energy of 0.91 eV was derived, it was in good agreement with a previous study by Fischer²¹ and also with the experimental value of 0.9 eV. An increase of the Frenkel defect concentration would explain the sudden increase in conductivity observed for this compound for temperatures higher than 925°C. This leads to a complete disorder of the oxygen vacancies above 1040°C, temperature at which the structure transforms to the cubic perovskite.

The structure of Bi_2WO_6 was described in the Pca_2_1 space group²² with the oxide ions located on six different crystallographic sites.

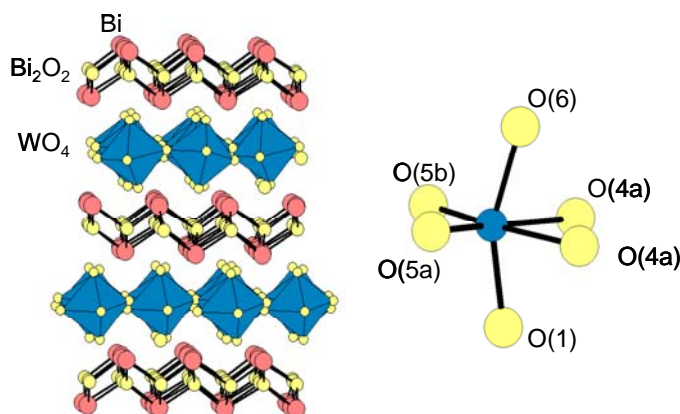


Figure 3. Bi_2WO_6 structure

To derive preferential oxygen diffusion pathways, an intermediate state, with an oxide ion placed between two oxygen vacancies, was considered. The resulting migration energies of a range of oxygen jumps are reported in table 1.

Table 1. Energies of oxygen migration in Bi_2WO_6

migration pathways	E_{mig}/eV	migration pathways	E_{mig}/eV
WO_6 (apical-equatorial)		WO_6 (equatorial-equatorial)	
O(1)-O(4a)	0,97	O(4a)-O(4b)	1,67
O(1)-O(4b)	0,45	O(4a)-O(5b)	1,61
O(1)-O(5a)	1,73	O(4b)-O(5a)	2,71
O(1)-O(5b)	0,63	O(5a)-O(5b)	1,67
O(6)-O(4a)	0,63		
O(6)-O(4b)	1,73	Bi_2O_2 sheets	
O(6)-O(5a)	0,45	O(2)-O(2)	1,60
O(6)-O(5b)	0,97	O(3)-O(3)	1,60

With a migration energy of 1.6eV, the diffusion of oxide ion within the Bi_2O_2 layers is difficult. The low energy pathway involves a zigzag type mechanism between adjacent apical O(1,6) and equatorial O(4,5) sites, with an alternative sequence of migration energies of 0.45 and 0.63eV. In view of this type of motion, highly anisotropic ionic conductivity was expected with an activation energy of 0.63eV. An activation energy of 0.6eV was derived above 500°C from impedance spectroscopy in good agreement with this calculated value. To explain the increase of the activation energy at temperature below 500°C, defect association was considered. The formation of a dopant-vacancy cluster would lead to an additional binding energy of 0.25eV, in good agreement with the experimental value of 0.75eV. It was then proposed that the observed slope change in the ionic conductivity could be related to dopant-vacancy association at low temperature. In case of bismuth based compounds, rather low activation energies are usually observed (0.2 eV for $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ and 0.5eV for Bi_2WO_6 derivatives against 1eV for Brownmillerite). The lone pair of bismuth ions, strongly polarizable, is likely responsible for this, inducing an additional interaction which contributes to push back the ions from one site to another²³.

OXYGEN TRANSPORT AT THE SCALE OF A UNIT CELL

The anisotropic conductivity of these materials was confirmed by neutron diffraction which evidenced a high disorder of the oxide ions in the vanadium slabs of BIMEVOX and in the tetrahedral layers of the Brownmillerite. To take into account the whole density of nucleons of the oxide ions, an anharmonic tensor was used to model the thermal motion.

The Probability Density Function (PDF) of the oxygen nucleons around the vanadium atoms in the structure of $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ at 700°C is given in the following figure. From these PDF, pseudo-potentials were derived. Several possible oxygen pathways were considered and the lowest barrier of energy was obtained for the diffusion of an oxygen from an apical oxygen site towards an equatorial oxygen in the surrounding of the vanadium ion. It led to a value of 0.16eV in good agreement with the experimental value of 0.2eV measured by impedance spectroscopy.

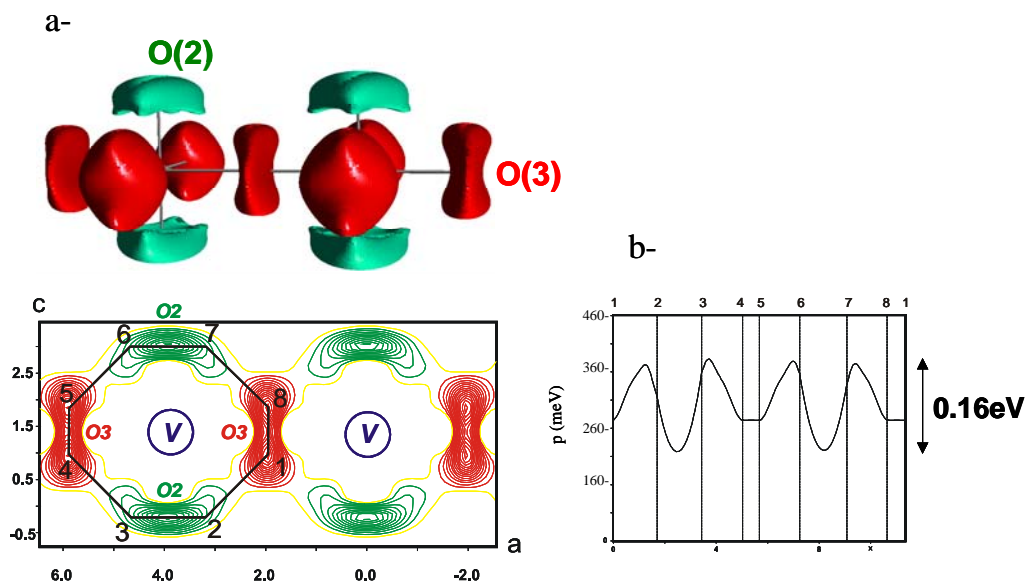


Figure 4. a) Probability Density Function of oxygen nucleons around the vanadium atoms in the structure of γ - $\text{Bi}_4\text{V}_2\text{O}_{11}$ at 700°C b) and derived pseudo-potential

Neutron diffraction was also performed on $\text{Ba}_2\text{In}_2\text{O}_5$ derived compounds. Data were collected at 700 and 950°C for composition $\text{Ba}_2\text{In}_{2-x}\text{Mo}_x\text{O}_{5+3x/2}$ with $x=0.1$. The symmetry of this compound is orthorhombic at room temperature, it becomes tetragonal at 600°C and then cubic above 925°C . The tetragonal form at 700°C can be described as a double perovskite corresponding to the intergrowth of octahedral In(1) layers and oxygen deficient In(2) layers. The refinement of the occupancy revealed that molybdenum was preferentially in the In(2) sites. To take into account all the nucleon density of oxygen atoms, an anharmonic model of the thermal motion was also used. The PDF of oxygen nucleons around the indium atoms is given in the next figure. Whereas an important disorder of the oxide ions was observed in the In(2) layers, it was less in the In(1) layers, thus confirming, at this temperature, a two-dimensional mechanism of oxygen diffusion in the oxygen deficient layers. Considering several different oxygen diffusion pathways, the lowest barrier of energy was observed for the jumps from an equatorial site to an adjacent equatorial site in the In(2) layers with a barrier of 0.4eV while a barrier of 0.6eV was calculated for a jump from an equatorial site to an apical site.

At 950°C , a barrier of energy of 1.1eV was deduced. The stabilization of the high temperature forms at lower temperature was confirmed by impedance spectroscopy. The value of 1.1eV derived from the neutron diffraction study at 950°C was in good agreement with the experimental value of 1.03eV observed for the same composition at temperature above 700°C , in contrast to the value of 0.4eV deduced at 700°C . Diffusion at long distance in ceramics is more complex than diffusion at the atomic scale. Other barriers to the diffusion, such as grain boundaries, have to be taken into account. Moreover, one must be careful with the use of these pseudo-potentials since they give only a qualitative information on the possibility of migration and suppose a dynamic disorder of oxide ions. Indeed, one cannot exclude the possibility that the spreading of the nucleon density observed at 700°C would be the result of the superimposition of different oxygen surrounding of indium atoms instead of a dynamic disorder.

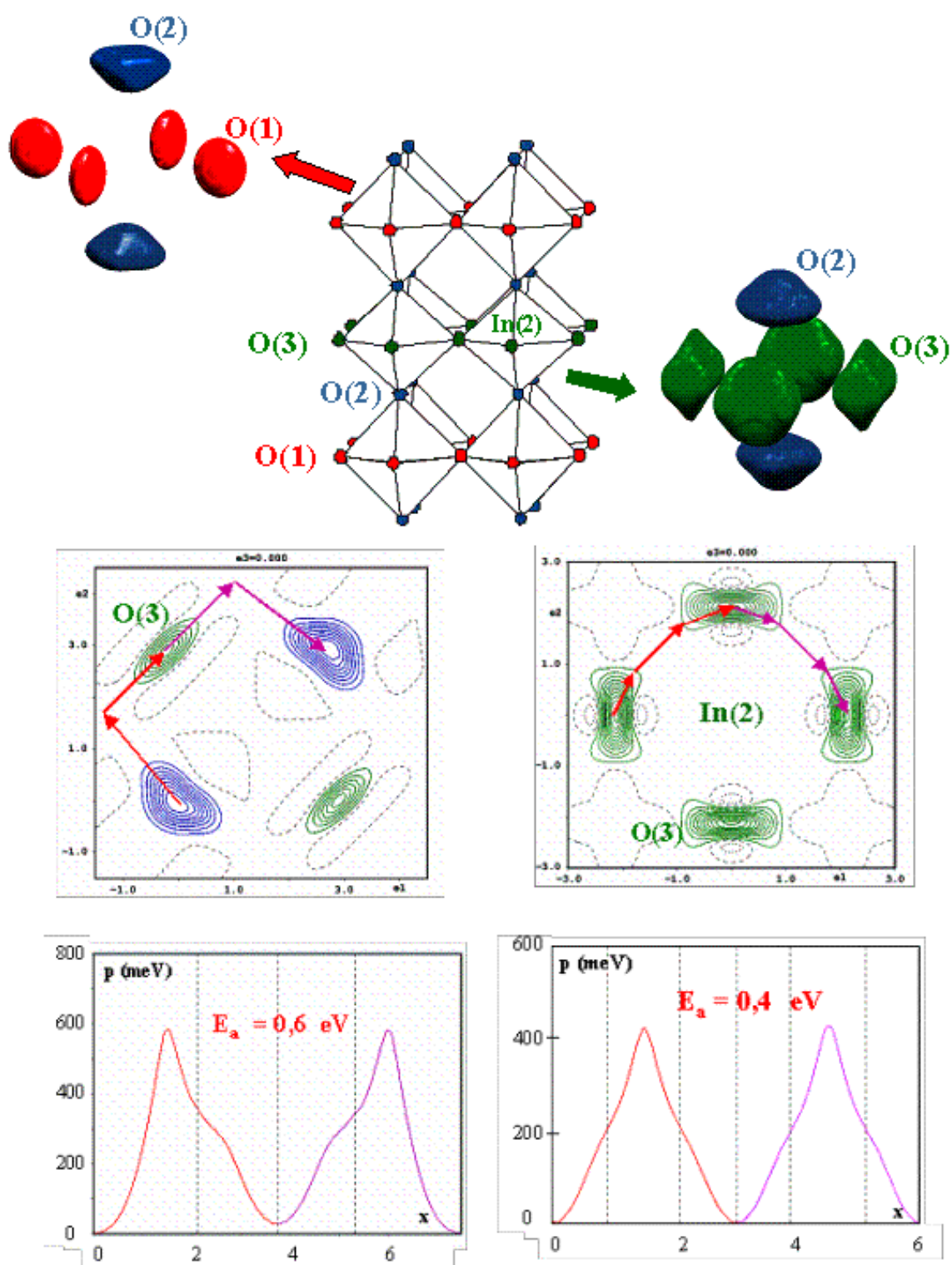


Figure 5. a) Probability Density Function of oxygen nucleons around the indium atoms in the structure of $\text{Ba}_2\text{In}_{2-x}\text{Mo}_x\text{O}_{5+3x/2}$ with $x=0,1$ at 700°C

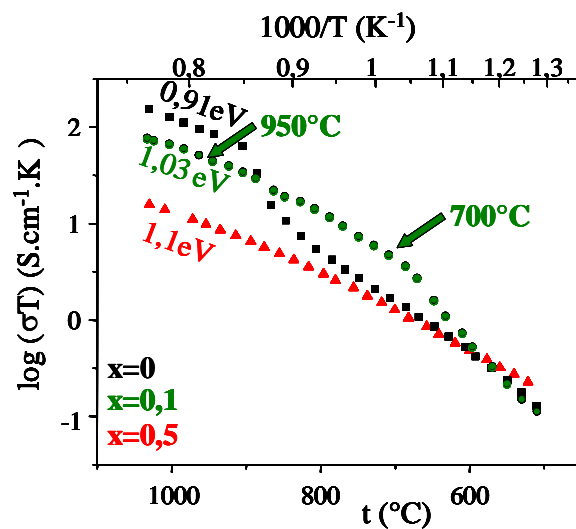


Figure 6. Arrhenius plot of the conductivity of $\text{Ba}_2\text{In}_{2-x}\text{Mo}_x\text{O}_{5+3x/2}$ with $x=0, 0.1$ and 0.5

OXYGEN TRANSPORT AT THE CERAMIC SCALE

For the applications, dense ceramics are needed. If ceramics with relative density higher than 95% were easily obtained for the BIMEVOX^{24, 25}, we did not succeed in optimizing density of the Brownmillerite phases. These compounds absorb and then desorb water between 100 and 400°C, which complicates their densification. Their conductivities were measured on ceramics with relative density ranging between 60 and 80%.

BIMEVOX materials were tentatively developed as membrane for the electrically driven separation of oxygen from air. Faradic yields close to 100% with current density up to $2\text{A}\cdot\text{cm}^{-2}$ ($1\text{A}\cdot\text{cm}^{-2}$ is equivalent to $3.5\text{cm}^3\cdot\text{min}^{-1}$) were obtained with membranes simply made of a dense BIMEVOX ceramic, sandwiched between two gold grids, used as current collector^{26,27}. In contrast, low oxygen permeation was observed when membranes were placed between two different atmospheres of oxygen^{28,29}.

Permeation is not only a function of the ionic conductivity but also of the electronic conductivity, and a too small electronic conductivity may explain these very low fluxes. However permeation was not improved with a 40% gold cermet. Another parameter which governs the transport of oxygen in a ceramic is the kinetics of the molecular exchange (dissociation of oxygen molecule into oxide ions and recombination of these ions into molecule) at the surface. To characterize the oxygen transport in these ceramics, $^{18}\text{O}/^{16}\text{O}$ isotope exchanges were performed and the profiles of penetration of ^{18}O were measured by Secondary Ions Mass Spectrometry (SIMS). The high oxygen diffusion in these ceramics was confirmed. However, under dry atmosphere, very weak concentrations of oxygen were measured due to a very slow kinetic of surface exchange. The kinetic was improved under a wet atmosphere³⁰. The same experiments were carried out under a current bias, applied between two gold electrodes. Under bias, the oxygen transfer was considerably increased³¹. An in-situ X-ray diffraction study of these membranes under current polarization revealed a slight reduction of the ceramic under bias which was almost reversible when the current was turned off³². Under bias, the vanadium, V^{V} , is slightly reduced into vanadium, V^{IV} , the electronic conduction is thus enhanced and the oxygen transfer at the surface is then increased. However, without a careful control of the electrical potential, a reduction of bismuth may occur and limit the application of these materials.

CONCLUSION

BIMEVOX were evidenced in our lab about 20 years ago. By combining several techniques, we manage to understand their transport of oxygen from the atomic scale to the macroscopic scale. They are fast oxide ion conductors because of their layered structure, their intrinsic oxygen vacancies and this specificity of bismuth ion which possesses a lone pair which contributes to the diffusion process and is likely the cause of the low activation energies observed for bismuth based oxide ion conductors. Unfortunately the main drawback of these materials is their lack of stability under reducing atmosphere which considerably limits their range of application. We applied the same techniques to $\text{Ba}_2\text{In}_2\text{O}_5$ derivatives but were limited by problems of densification. The research of new oxide ion conductors, as stable as stabilized zirconia, with better conductivity, still remains a challenge.

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