



HAL
open science

Ionic conductivity in sheet oxides

Claude Delmas, Mohamed Maazaz, Claude Fouassier, Jean-Maurice Réau, Paul Hagenmuller

► **To cite this version:**

Claude Delmas, Mohamed Maazaz, Claude Fouassier, Jean-Maurice Réau, Paul Hagenmuller. Ionic conductivity in sheet oxides. P. Vashishta; J. N. Mundy; G. S. Shenoy. Fast ion transport in solids, electrodes and electrolytes, Elsevier, pp.451-454, 1979, ISBN, 0-444-00353-3. <hal-00134915>

HAL Id: hal-00134915

<https://hal.science/hal-00134915v1>

Submitted on 21 Sep 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

IONIC CONDUCTIVITY IN SHEET OXIDES

C. Delmas, A. Maazaz, C. Fouassier, J.M. Réau and P. Hagemuller

Laboratoire de Chimie du Solide du C.N.R.S.

Université de Bordeaux I

351 cours de la Libération, 33405 Talence, Cedex, France.

ABSTRACT

A new class of alkali ionic conductors with sheet structures has been found. The two families $A_x(L_xM_{1-x})O_2$ ($L = \text{In, Sc}; M = \text{Zr, Hf, Sn, Pb}$) and $A_x(L_{x/2}Sn_{1-x/2})O_2$ ($L = \text{Mg, Ca, Zn}$) ($A = \text{Na, K}$) ($x \leq 1$) have been studied. In all those new layered materials the lattice is built up by sheets of edge-sharing $(L, M)O_6$ octahedra between which the alkali ions are intercalated, with trigonal prismatic or octahedral environment. The mobility of the alkali ions can be discussed on the basis of their environment and the electronegativity of the L and M elements. The results show that the mobility is strongly correlated to the environment of the alkali ions : when the mobile ion is in a trigonal prismatic site the conductivity is 3 or 4 orders of 10 higher than when it is in an octahedron.

INTRODUCTION

In recent years we have prepared several families of sheet oxides with the formula A_xMO_2 ($A = \text{Na, K}; M = \text{Cr, Mn, Co}$) ($0.5 \leq x \leq 1$) [1]. Their structures can be classified into three groups, but they are all characterized by a packing of $(MO_2)_n$ sheets between which the alkali atoms are intercalated. These structures are similar to those obtained for transition chalcogenides and their intercalates [2]. While in such materials the weak repulsions between adjacent chalcogenide layers allow a very wide range for x ($0 \leq x \leq 1$), in oxides the higher ionic character of the bonds requires $x > 0.5$. The vacancy concentration is equal to $1-x$ and a 2D ionic motion can be expected in these materials. However all non-stoichiometric phases have an important electronic conductivity. The same element is present in two different oxidation states in equivalent sites. According to the overlap of the t_{2g} orbitals the d electrons are more or less delocalized (the A_xCoO_2 phases are metallic, but K_xCrO_2 and A_xMnO_2 are semi-conductors).

To get a pure ionic conductor one has to suppress the electronic component of the conductivity. We have done this by substitution of the transition element in the sheets by a couple of diamagnetic ions having different oxidation states. This leads to a formulation $A_x(L, M)O_2$.

In this paper we describe two families of sheet oxides which are simultaneously ionic conductors and electronic insulators and we discuss

the influence of structural parameters and the nature of bonding on the mobility of the alkali ion.

CRYSTAL CHEMISTRY

According to the nature of the L and M ions two series of materials can be obtained : If L and M are respectively trivalent and tetravalent the phases may be formulated $A_x(L_x^{III}M_{1-x}^{IV})O_2$. We have investigated this family with $L = \text{Sc, In}$ and $M = \text{Zr, Hf, Sn, Pb}$ [3]. If L and M are divalent and tetravalent respectively, phases with the formula $A_x(L_{x/2}^{II}M_{1-x/2}^{IV})O_2$ are obtained. Such systems have been explored for $L = \text{Mg, Ca, Zn}$, and $M = \text{Sn}$ [4].

Figure 1 shows the composition of the different sheet oxides obtained in these two series. Obviously it is difficult to get non-stoichiometric layered structures with sodium. All attempts failed except in the case of

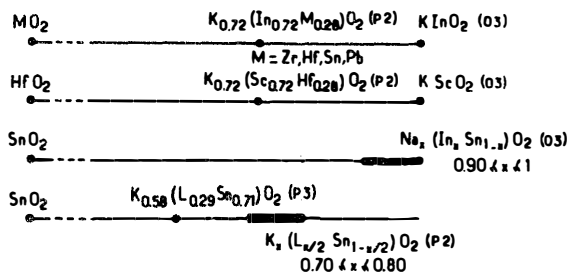


FIG. 1: Compositions of the $A_x(L, M)O_2$ phases

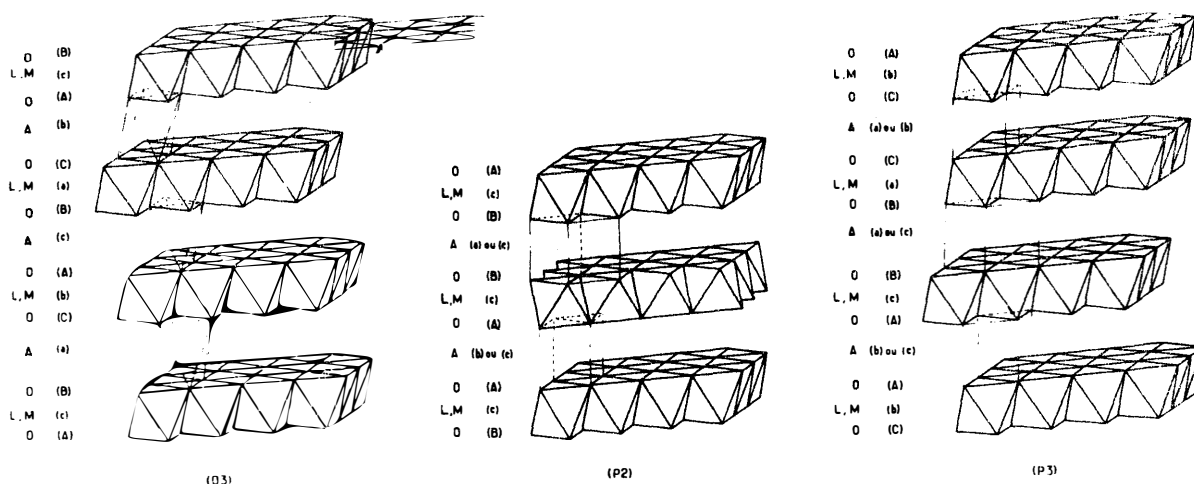


FIG. 2 : Different types of packings in layered oxides

$\text{Na}_x(\text{In}_x\text{Sn}_{1-x})\text{O}_2$. Lamellar sodium phases are obtained with 3d elements, probably because of the small size of the 3d ions which causes a polarization of the oxygen atoms and a higher covalency of the M-O bond. Likely the large size of the diamagnetic ions (Sn^{4+} , In^{3+} , Zn^{2+} , Ca^{2+} ...) does not permit a strong polarization of the oxygen and consequently the layered structure can exist only when big alkali ions separate the oxygen layers.

As shown in Fig. 1 three types of layer structures (O3, P2 and P3) are obtained in the potassium systems [1]. They are drawn in Fig. 2. In each case the (L, M) O_2 sheets are built up by edge-sharing octahedra.

The three types differ only by the sequence of the sheets. As a consequence two types of environments are obtained for the alkali ion. The trigonal prismatic environment is the most common; octahedral coordination is only observed for weak vacancy content ($x \geq 0.9$).

IONIC CONDUCTIVITY

The study of the ionic conductivity has been performed by complex impedance measurements on sintered pellets. Ionically blocking electrical contacts are obtained by evaporation of gold under vacuum. Fig. 3 and Fig. 4 show plots of $\log \sigma$ vs reciprocal temperature for several layer oxides. Table I lists the activation energy and the conductivity obtained at 500 K for these materials.

From these data two principal findings can be derived :
 - the nature of the environment of the alkali ion (octahedral or trigonal prismatic) is the main parameter influencing the conductivity
 - the mobility of the alkali ion can be correlated with the covalent character of the sheets.

These two points will be developed in the following sections.

Influence of the environment of the alkali ions

The comparison of conductivity data of $\text{Na}_x(\text{In}_x\text{Sn}_{1-x})\text{O}_2$ and KInO_2 in which alkali ions are intercalated in an octahedral environment, and of $\text{K}_{0.72}(\text{In}_{0.72}\text{Sn}_{0.28})\text{O}_2$ characterized by a trigonal prismatic environment of potassium suggests a difference in size of the different bottlenecks. In other words, the variation of

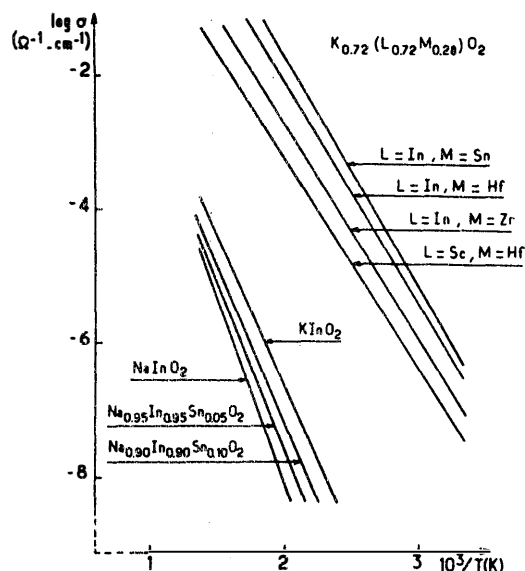


FIG. 3 : Variation of the logarithm of conductivity vs reciprocal temperature for $\text{A}_x(\text{L}^{\text{III}}, \text{M}^{\text{IV}})\text{O}_2$ phases

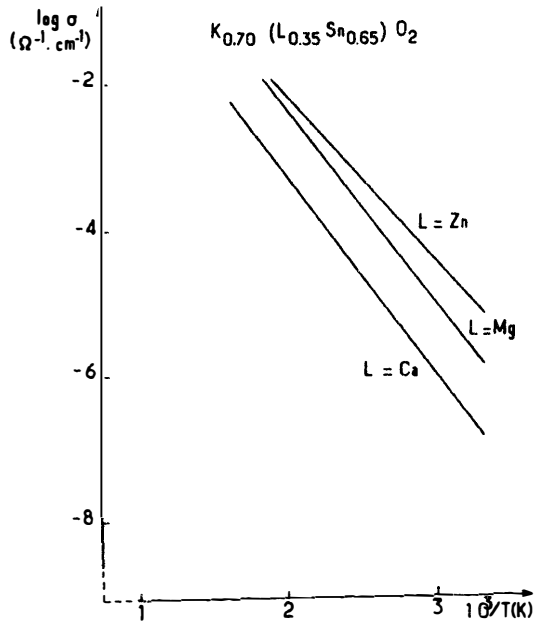


FIG. 4 : Variation of the logarithm of conductivity vs reciprocal temperature for $A_x(L^{II}, Sn)_2O_2$ phases

the A-O distance when an A^+ ion moves from one site to the neighbouring one can explain this difference in behaviour [5].

As shown in Fig. 5, for an octahedral environment, the ionic transport requires that the A^+ cations pass through an empty tetrahedron. Therefore, between two equivalent sites there are two triangular bottlenecks. On the contra-

TABLE I : Conductivities at 500 K and activation energies for $A_x(L,M)_2O_2$ phases.

	$\sigma_{500\text{ K}}$ ($\Omega^{-1} \cdot \text{cm}^{-1}$)	ΔE (eV)
$K_{0.72}(In_{0.72}Zr_{0.28})O_2$	$2.2 \cdot 10^{-3}$	0.65
$K_{0.72}(In_{0.72}Hf_{0.28})O_2$	$1. \cdot 10^{-2}$	0.67
$K_{0.72}(In_{0.72}Sn_{0.28})O_2$	$2.2 \cdot 10^{-2}$	0.69
$K_{0.72}(Sc_{0.72}Hf_{0.28})O_2$	$5.6 \cdot 10^{-4}$	0.62
$K_{0.70}(Mg_{0.35}Sn_{0.65})O_2$	$5.0 \cdot 10^{-3}$	0.52
$K_{0.70}(Ca_{0.35}Sn_{0.65})O_2$	$6.3 \cdot 10^{-4}$	0.54
$K_{0.70}(Zn_{0.35}Sn_{0.65})O_2$	$7.9 \cdot 10^{-3}$	0.45
$NaInO_2$	$7.9 \cdot 10^{-9}$	1.09
$Na_{0.90}(In_{0.90}Sn_{0.10})O_2$	$6.3 \cdot 10^{-8}$	0.93
$KInO_2$	$2.5 \cdot 10^{-7}$	0.87

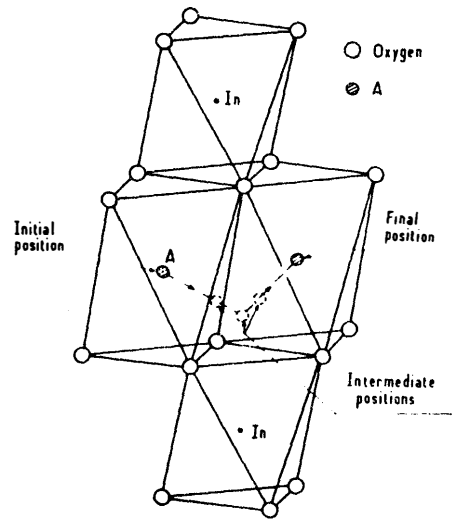


FIG. 5 : Diffusion path of the alkali ion in octahedral environment

ry when the alkali ion is in a trigonal prism (Fig. 6) there are two rectangular bottlenecks and the intermediate site is another trigonal prism.

From the cell parameters and the indium-oxygen bond lengths ($d_{In-O} = 2.155 \text{ \AA}$ [6]) we have calculated the R ratio of the cation-anion distance during diffusion to that inside of the original polyhedron [7]. We can admit that the value $1-R$ characterizes the steric bulk part of the activation energy. In Fig. 7 we have plotted the values of $1-R$ for octahedral and trigonal prismatic environments of the alkali ion.

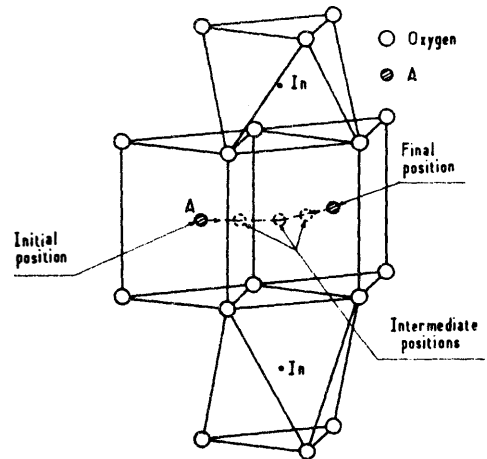


FIG. 6 : Diffusion path of the alkali ion in trigonal prismatic environment

These curves show on one hand that the steric interaction is greater in NaInO_2 than in KInO_2 , in agreement with the conductivity curves, and on the other hand that the A-O distance variation is much less pronounced for the trigonal prismatic environment than for the octahedral one. This accounts for the high conductivity of $\text{K}_{0.72}(\text{In}_{0.72}\text{Sn}_{0.28})\text{O}_2$. In the case of layered sulfides, L. Trichet and J. Rouxel have also observed the highest mobilities when the alkali ions occupy trigonal prisms [8].

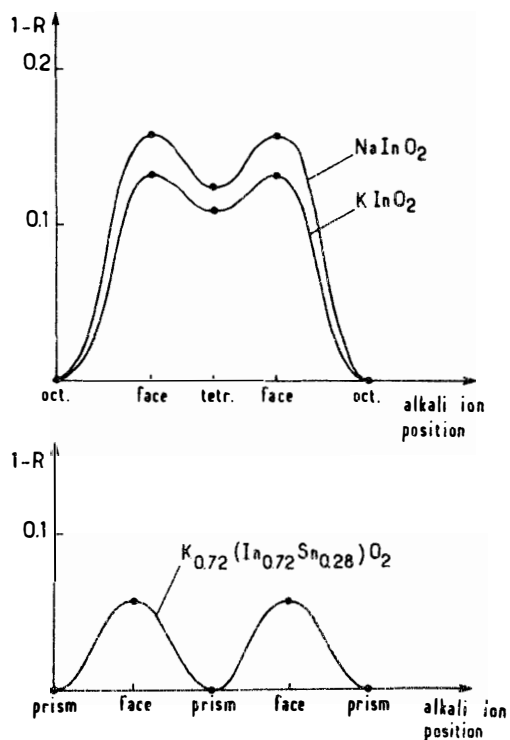


FIG. 7 : Variation of the steric part of the activation energy during the diffusion

Correlation between mobility and covalent character of the sheets

As Fig. 3 and Table I show clearly, in the $\text{K}_{0.70}(\text{L}_{0.35}^{\text{II}}\text{Sn}_{0.65}^{\text{IV}})\text{O}_2$ phases (L = Ca, Mg, Zn) the mobility of the alkali ion increases from calcium to zinc. The electronegativity and therefore the covalency of the (L, M)-O bonds (calculated from the Pauling formula [9]) increase in the same order. The greater the covalency of the sheets, the lower the electro-

static interactions between the mobile cation and its anionic environment will be and as a consequence the higher the mobility.

Such an effect of the covalency has been also reported by J. Rouxel and coworkers in the case of isostructural sulfides [8, 10]. The activation energy in these materials is significantly below that of oxides because the M-X (X = S, Se, Te) bonds are more covalent.

For $\text{K}_{0.72}(\text{L}_{0.72}^{\text{III}}, \text{M}_{0.28}^{\text{IV}})\text{O}_2$ phases the conductivity increases with the covalency of the sheets, but the activation energy increases slowly from 0.62 eV to 0.69 eV. The activation energy of the $\text{A}_x(\text{L}_{1-x}^{\text{II}}, \text{M}_{1-x}^{\text{IV}})\text{O}_2$ series, which is between 0.45 eV and 0.54 eV, is significantly below that of the $\text{A}_x(\text{L}_x^{\text{III}}, \text{M}_{1-x}^{\text{IV}})\text{O}_2$ phases. All these results suggest the influence of another parameter on the activation energy. We have shown that for $\text{K}_{0.72}(\text{In}_{0.72}\text{Sn}_{0.28})\text{O}_2$ the sheets were rippled (indium and tin atoms are not at the same z value) [11]. This deformation of the sheets probably increases the activation energy. It can also be emphasized that in these phases the number of A^+ and L^{III} ions are equal. Such a composition can stabilize a more ordered distribution and thus decrease the mobility.

REFERENCES

1. C. Fouassier, C. Delmas and P. Hagenmuller, *Mat. Res. Bull.*, **10**, 443 (1975).
2. A. Leblanc-Soreau, M. Danot, L. Trichet and J. Rouxel, *Mat. Res. Bull.*, **9**, 191 (1974).
3. C. Delmas, C. Fouassier, J.M. Réau and P. Hagenmuller, *Mat. Res. Bull.*, **11**, 1081 (1976).
4. A. Maazaz, C. Delmas, C. Fouassier, J.M. Réau and P. Hagenmuller, *Mat. Res. Bull.*, **14**, 193 (1979).
5. *Solid Electrolytes*, ed. P. Hagenmuller and W. Van Gool, Academic Press, 1978.
6. Von E. Hubbert-Paletta, R. Hoppe and G. Kreuzburg, *Z. anorg. allg. Chem.*, **379**, 255 (1970).
7. R.D. Armstrong, R.S. Bulmer and T. Dickinson, *Fast Ion Transport in Solids*, *Belgirate Colloq.*, W. Van Gool ed., p. 269 (1972).
8. L. Trichet and J. Rouxel, *Mat. Res. Bull.*, **12**, 345 (1977).
9. L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell Univ. Press (1960).
10. J. Rouxel, *Mat. Res. Bull.*, **13**, 1425 (1978).
11. C. Delmas and P.E. Werner, *Acta Chem. Scand.*, **A32**, 329 (1978).