

Sensing Behavior of Vanadates and Molybdates under Low Oxygen Partial Pressures at 1,000°C*

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Vanadate and molybdate ceramics reproducibly showed a drastic reduction of electrical resistivity over 10^8 ($\Omega \cdot \text{cm}$) or more under the oxygen partial pressure ranging $10^{-11} \sim 10^{-17}$ (atm) at 1000°C. This large step-wise change in resistivity was found to arise from the phase transition between the insulating phases as AMO_4 (A=Ba, Sr, La, Sm, Y; M=V, Mo) and the high conducting phases as AMO_3 . Use of these oxides for fabrication of oxygen sensors or the calibrating materials for a zirconia cell was discussed.

INTRODUCTION

In recent years, some oxygen sensors have been presented for the monitoring and control of the combustion process in an internal combustion engine or a furnace¹⁻⁴. All of these sensors operate by virtue of the gradual variation in electrical resistivity proportional to the ambient oxygen partial pressure (P_{O_2}). If a step-wise change of resistivity in oxide ceramics takes place with changing P_{O_2} , it will serve to indicate directly the value of the oxygen partial pressure in terms of its jumping point.

The present author discovered a quick phase change with dissociating O_2 gas from BMoO_4 (sheelite-type oxide; B=alkaline-earth metals) to BMoO_3 (perovskite-type oxide) under the oxygen partial pressure in the range $10^{-12} \sim 10^{-16}$ atm at 1200°C⁵. The BMoO_4 compounds behave as a pure insulator with no conduction electrons, whereas the BMoO_3 compounds show

a metallic conduction with $4d^2$ electrons⁶. Similarly, LnVO_4 (Ln=La, Sm, Y) compounds belong to an insulator, while LnVO_3 compounds show a good conduction with $3d^2$ electrons⁷. Table 1 summarizes some physical properties, partially derived from previous reports, for AMO_4 (A=Ba, Sr, La, Sm, Y; M=V, Mo) and AMO_3 compounds⁶⁻⁹. The resistivity of AMO_4 compounds was roughly measured by the present author using the 2-probe method owing to lack of experimental data. In the present work, the possibility of a new oxygen sensor using vanadates and molybdates was reported.

EXPERIMENTAL

Appropriate mixtures between the alkaline-earth nitrates (or rare-earth oxides) and MoO_3 (or V_2O_5) were pressed and heated in air at 1200°C in order to obtain the molybdates (BaMoO_4 , SrMoO_4) and the vanadates (LaVO_4 , SmVO_4 , YVO_4). A small piece (about $5 \times 3 \times 3$ mm) was cut out from the sintered disk of ceramics. The piece attached Pt wires with Pt

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Table 1 Physical properties for AMO_4 and AMO_3 compounds

Compound	Structure	$\rho \cdot \text{cm}$ 1000°C	Compound	Structure	$\rho \cdot \text{cm}$ 1000°C
BaMoO_4	sheelite	$\sim 10^9$	BaMoO_3	perovskite	10^{-4} metallic
SrMoO_4	sheelite	$\sim 10^9$	SrMoO_3	perovskite	10^{-4} metallic
LaVO_4	huttonite	$\sim 10^9$	LaVO_3	perovskite	$10^{-2.1}$ semi.
SmVO_4	zircon	$\sim 10^9$	SmVO_3	perovskite	$10^{-0.2}$ semi.
YVO_4	zircon	$\sim 10^9$	YVO_3	perovskite	$10^{1.1}$ semi.

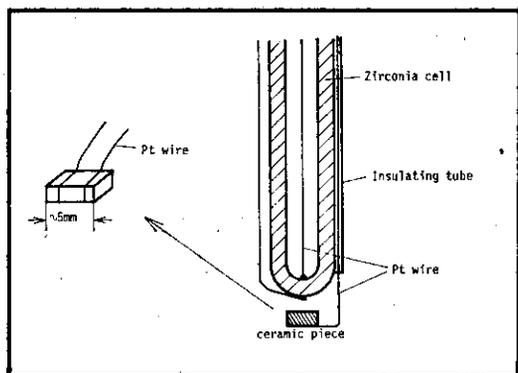


Fig. 1 Aspect of the ceramic piece and zirconia cell

paste as electrodes was fixed near the top of a zirconia cell for P_{O_2} measurement as in Fig. 1. A furnace, in which the zirconia cell was set, was maintained at 1000°C and the $\text{H}_2\text{-CO}_2$ mixed gas was introduced in order to control P_{O_2} ranging $\log P_{O_2}$ (atm) = $0 \sim -18$. The oxygen partial pressure in the furnace was measured using the zirconia cell. During the measurement for resistivity by the 2-probe method, the P_{O_2} in the furnace was gradually decreased at 1000°C . X-ray powder diffraction ($\text{CuK}\alpha$)

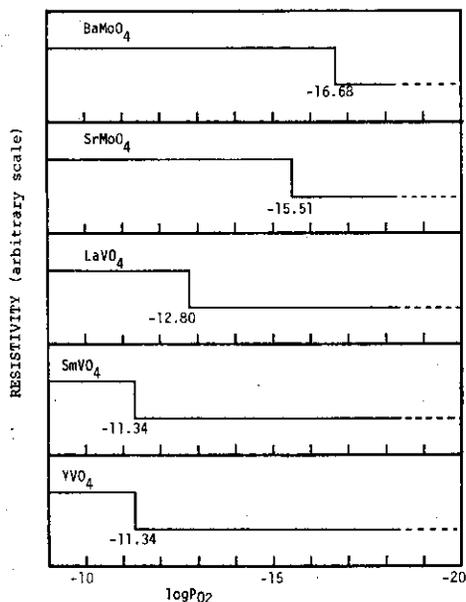


Fig. 2 Relationship between resistivity and oxygen partial pressure for molybdates and vanadates at 1000°C

and thermogravimetry were carried out so as to identify the solid phases.

RESULTS AND DISCUSSION

Fig. 2 schematically shows the conducting behavior of each compound by the 2-probe method. The ordinates were designated in arbitrary scales because the 2-probe method could not measure exactly the absolute values of resistivity, particularly in a low resistivity range. In the high resistivity region of AMoO_4 , each compound showed constant values of resistivity about $10^8 \sim 10^{10}$ ($\Omega\text{-cm}$), respectively, in spite of decreasing P_{O_2} . However, these insulating behaviors of AMoO_4 changed into the metallic ones at certain values of P_{O_2} . Fig. 2 indicates the oxygen partial pressures, which bring about a significant change in resistivity over 10^8 ($\Omega\text{-cm}$) or more, to be $10^{-16.68}$ atm (BaMoO_4), $10^{-15.51}$ atm (SrMoO_4), $10^{-12.80}$ atm (LaVO_4), $10^{-11.34}$ atm (SmVO_4) and $10^{-11.34}$ atm (YVO_4), respectively. The decrease in resistivity for all compounds was so rapid that a stationary value was observed within 20 or 30 seconds. However, increasing rates of resistivity in the oxidizing direction were rather slow. Thus, the molybdate or vanadate pieces with the function of a switching element could repeat undoubtedly on-off action in several cycles with changing P_{O_2} . In order to know a more detailed feature in re-

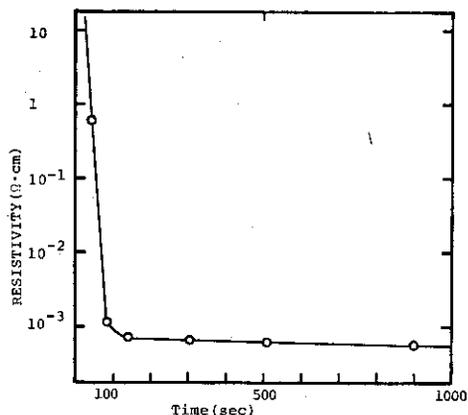


Fig. 3 Variation of resistivity of SrMoO_4 with time at $\log P_{O_2} = -15.51$ and 1000°C

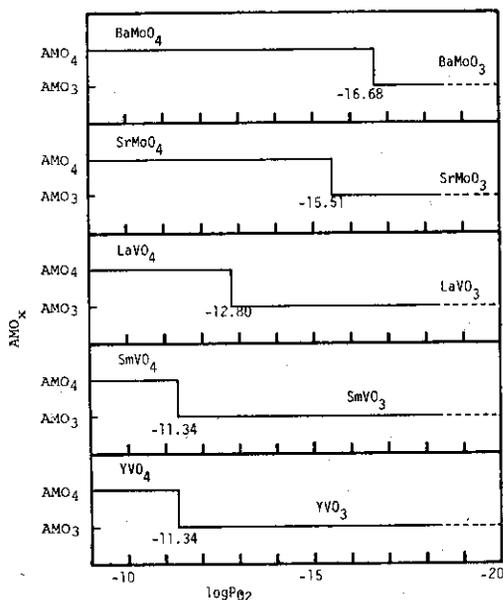


Fig. 4 Thermogravimetric result for molybdates and vanadates at 1000°C

sistivity, the 4-probe measurement was undertaken for SrMoO_4 at 1000°C and $P_{\text{O}_2} = 10^{-15.51}$ (atm) as shown in Fig. 3. It took less than 100 seconds from an introduction of the mixed gas of $P_{\text{O}_2} = 10^{-15.51}$ (atm) into the furnace till descent in resistivity. This response time of the piece was shorter than that of the zirconia cell. The other compounds showed almost the same behaviors of resistivity as SrMoO_4 . Subsequently, the results of X-ray powder diffraction and thermogravimetry revealed all AMO_4 and AMO_3 compounds to be just linear phases as interpreted from Fig. 4. The P_{O_2} of the transition point between AMO_4 and AMO_3 phases in Fig. 4 was accurately consistent with that of the transition point of resistivity in Fig. 2.

Now, considering the system AMO_4 , AMO_3 and O_2 , the reaction equilibrium is established as follows.



From the Gibbs phase rule, the system at equilibrium has only one degree of freedom ($F=1$). Thus, if temperature is arbitrarily fixed, P_{O_2} is

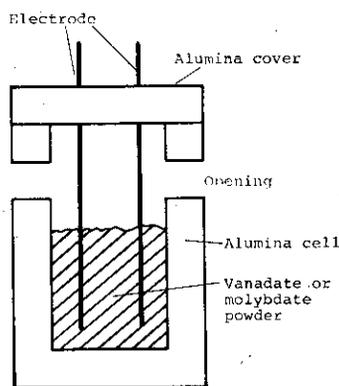


Fig. 5 Oxygen sensing cell charged with molybdate or vanadate powder

fixed. Hence, these oxide ceramics can be served not only as oxygen sensors with a switching function, but also as calibrating materials which check the deterioration of zirconia cells¹⁰⁻¹³.

The ceramics pieces prepared in this work unexpectedly showed small cracks after a few tens cycles owing to a difference in density between AMO_4 and AMO_3 . A container charged with vanadate or molybdate powder, as shown in Fig. 5, may be considered to be good for repeated use.

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