JOURNAL OF SOLID STATE CHEMISTRY **130,** 316–318 (1997)
ARTICLE NO. SC977297

BRIEF COMMUNICATION

A New Series of Co-Free Oxides with High Oxygen Permeability

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Received September 30, 1996; in revised form January 23, 1997; accepted January 28, 1997

A new series of oxides without Co elements, $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 4, 6, 8, 10$), was synthesized successfully. They have perovskite-like structures. These oxides have high oxygen permeability and lower thermal expansion coefficients. The oxygen permeation rate at 1150 K is 0.90 ml (STD)/cm^2 min for $n = 10$ and 0.41 ml (STD)/cm^2 min for $n = 6$. Their oxygen permeating behaviours are related with the Bi contents and their special structures. © 1997 Academic Press

Perovskite-type oxides, such as $La_{1-x}Sr_xCoO_3$ and $La_{1-x}Sr_xNiO_3$, have both high electronic conductivities and oxygen ion transport abilities. The membranes based on this kind of material are called the mixed conducting oxygen permeating membranes. The mechanism for oxygen permeation can be described as follows: the oxygen molecules in the high oxygen pressure side of the membrane are absorbed, transform to O^{2-} ions by partial oxidation of the transition oxide component of the membrane ($Ni^{+2} \rightarrow Ni^{+3}$) which are transported to the low–pressure side where the electron-transfer process is reversed, and neutral O atoms emerge (1–3). Compared with the electrolyte membranes, γ-Al_2O_3, and organic membranes, the mixed conducting oxygen permeating membranes have 100% selectivity to O^{2-}, high oxygen permeability, and some other advantages. Especially, there are transition-metal ions in the materials of the membranes and a lot of oxygen vacancies in their crystal lattice. The membranes perhaps have catalytic activities in some chemical reactions (1–4). Meanwhile, because the membranes can supply single oxygen atoms for the reactions, the oxidation level of the reaction can be controlled by controlling the oxygen permeate rate of the membranes. This is very important to the partial oxidation of low alkanes. For example, methane can be oxidized to formaldehyde, methanol, C_2-product, and syngas (a term for "synthetic gasoline" products used in catalytic chemistry) in the membrane reactors with different oxygen permeability. According to Balachandran *et al.*'s recent work (5), a methane conversion efficiency of 98% and CO selectivity of 90% have been observed in an oxygen permeable membrane reactor at 1150 K. Therefore this kind of membrane can be used widely in the direct and indirect conversion of methane.

However, the practical application of the oxygen permeable membranes has not been realized. The main reason perhaps is that the thermal expansion coefficients of the membranes containing Co elements are 10 times higher than those of inorganic ceramics. The sealing of this membrane to other ceramics or metals is very difficult. One of the keys therefore to the successful application is to find new oxygen permeable materials with lower thermal expansion coefficients. In this report, a new series of oxides without Co, $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 4, 6, 8, 10$), was synthesized successfully, and they have high oxygen permeability and lower thermal expansion coefficients.

EXPERIMENTAL

The oxides $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 4, 6, 8, 10$) were synthesized by solid reaction method. The mixtures of $SrCO_3$, Bi_2O_3, and Fe_2O_3 were heated at 1000–1300 K for 12 h to get the precursor of perovskite-like oxides. For preparing a pore-free disk to measure the oxygen permeability, the powder of each sample was compressed to disks with 15 mm diameter, and then sintered at 1200–1450 K for 12 h. The structures of samples were identified by X-ray diffraction.

The oxygen permeation rate through the disk was measured in the range from 800 to 1200 K with apparatus similar with that reported before (3). The sample was put on top of the alumina tube by a ceramic bonding agent. Ar gas was introduced through a quartz tube to sweep the permeated oxygen and transferred to a gas chromatography for analysis with a TCD detector, while the up surface of the disk was open to air. If the disk is not dense, or it is broken, a N_2 peak will be detected by the gas chromatography.

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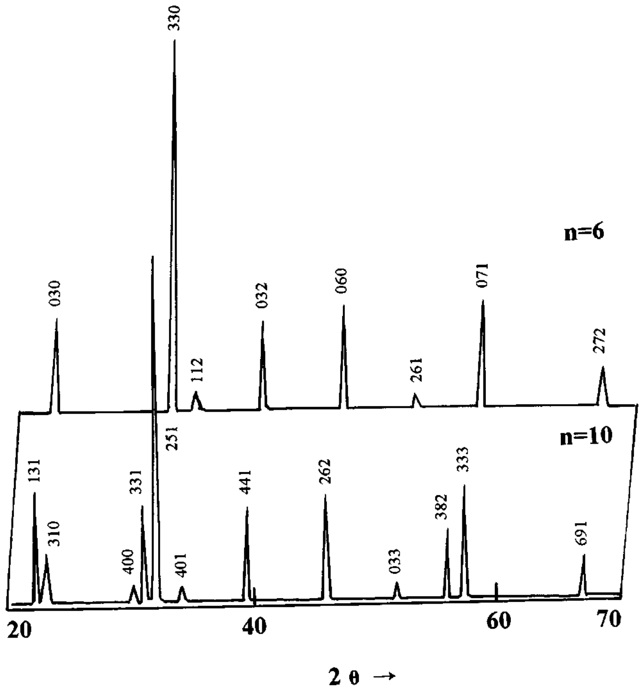

FIG. 1. The X-ray diffraction spectra of $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$ and 10).

RESULTS AND DISCUSSION

The X-ray diffraction spectra of $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$ and 10) are shown in Fig. 1. Their structures are very similar to those of perovskite-type oxides. When $n > 10$, some peaks of Fe_2O_3 can be observed in the spectra. This perhaps resulted from the volatilization of Bi_2O_3 at high temperatures. According to our calculation, the oxide $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$) crystallized in the tetragonal system with $a = b = 11.735$, $c = 5.503$, while $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 10$) crystallized in the orthorhombic system with $a = 11.705$, $b = 19.195$, $c = 5.513$. The X-ray diffraction data of $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$) are shown Table 1.

TABLE 1
The X-Ray Diffraction Data of $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$)

h	k	l	$d_{obs.}$	$d_{cal.}$	I/I_0
0	3	0	3.917	3.912	18
3	3	0	2.774	2.766	100
1	1	2	2.607	2.612	5
0	3	2	2.267	2.251	16
0	6	0	1.964	1.956	24
2	6	1	1.757	1.758	4
0	7	1	1.605	1.604	23
2	7	2	1.391	1.391	8

The new oxides $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$ and 10) with perovskite-like structures can be formulated as $Sr_{0.35}Bi_{0.3}Fe_{3-\&}$ ($n = 6$) and $Sr_{0.25}Bi_{0.5}FeO_{3-\&}$ ($n = 10$). This means that there is a high concentration of A-site vacancies in the new oxides, associated with oxygen vacancies needed to maintain charge balance.

Figure 2 shows the oxygen permeate flux versus temperature from 950 to 1250 K. The oxygen permeate rate of $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$) at 850°C is 0.41 ml (STD)/cm^2

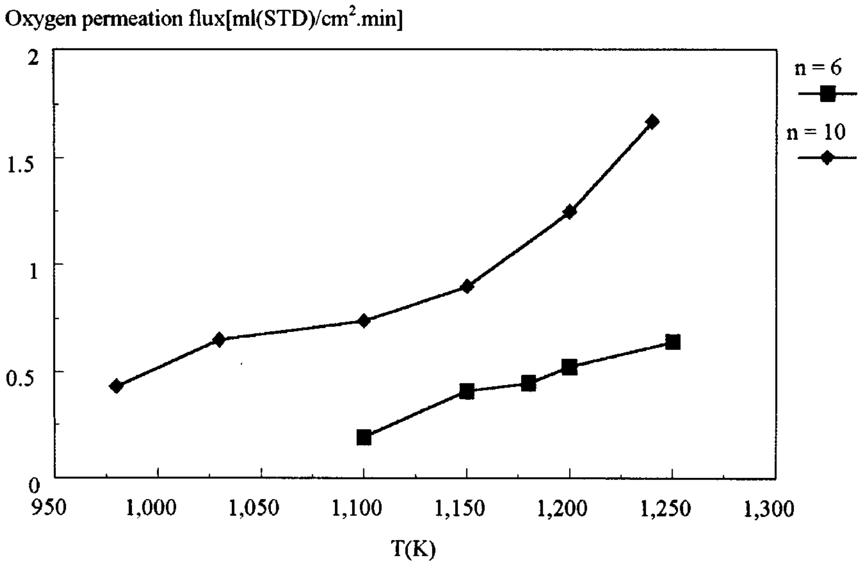

FIG. 2. The oxygen permeate flux of $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 6$ and 10) versus temperatures.

min, while that of $Sr_{10-n/2}Bi_nFe_{20}O_m$ ($n = 10$) is 0.90 ml (STD)/cm^2 min. This means that the oxygen permeability of the new oxides is equal to that of the Co-containing oxides, such as $La_{1-x}Sr_xCoO_3$ and $SrCo_{1-x}Fe_xO_3$, but much higher than that of the Mn-containing oxides, such as $La_{1-x}Sr_xMnO_3$ (3, 4). In other words, the new oxides are mixed conductors with high oxygen permeability.

The disks of the new oxides connected to alumina tubes by inorganic bonding agents are not broken when cooling from high temperatures, and they can be used repeatedly. But the disks of Co-containing oxides can be used only once and always break on cooling because of their high thermal expansion coefficients. This means that the thermal expansion coefficients of the new oxides are much smaller than those of the Co-containing oxides, but close to those of ceramics.

Above all, we have synthesized successfully a new series of Co-free oxides with high oxygen permeability and lower thermal expansion coefficients. Further experiments are in progress to understand the relation between their oxygen permeating behavior and their special structures.

ACKNOWLEDGMENT

This project was supported by National Natural Science Foundation of China and Natural Science Foundation of Liaoning.

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