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(54) Titre : MATIERE CERAMIQUE A BASE DE LANTHANIDES
(54) Title: LANTHANIDE CERAMIC MATERIAL

(57) Abrégé/Abstract:
A lanthanide oxide ceramic material is provided herein having the general formula $La_aLn_bM'_cM''_dO_{3-\delta}$. In such formula, Ln is a combination of Ce, Pr and Nd; M' is at least one alkaline earth metal; M'' is at least one metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr, and $0 \le a \le 1$; $0.01 < b \le 1$; $0 \le c \le 0.6$; $0 \le d \le 1$; and $-1 < \delta < +1$. Such material finds use as the ceramic material in a fuel cell.

ABSTRACT

A lanthanide oxide ceramic material is provided herein having the general formula $La_aLn_bM'_cM''_dO_{3-\delta}$. In such formula, Ln is a combination of Ce, Pr and Nd; M′ is at least one alkaline earth metal; M″is at least one metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr, and $0 \leq a \leq 1$; $0.01 < b \leq 1$; $0 \leq c \leq 0.6$; $0 \leq d \leq 1$; and $-1 < \delta < +1$. Such material finds use as the ceramic material in a fuel cell.

(a) TITLE OF THE INVENTION

LANTHANIDE CERAMIC MATERIAL

(b) TECHNICAL FIELD TO WHICH THE INVENTION RELATES

The present invention relates to a material based on a lanthanide-metal-containing, complex mixed oxide with functional electrical or catalytic properties exhibiting improved commercial and technical performance.

(c) BACKGROUND ART

Classical ceramic materials for solid oxide components, a variety of catalysts, electrical heating elements and other electronic ceramics are based on mixed oxides containing lanthanide elements such as perovskites having the general formula ABO_3. In this formula, the symbol A represents a single lanthanide element, and in some cases smaller amounts of alkaline earth metal elements. The symbol B represents a metal ion with an ionic radius smaller than the A cation. Changing the chemical composition makes it possible to control a variety of technologically important properties, e.g., electronic conductivity, ionic conductivity, heat conductivity, thermal expansion, catalytic properties, chemical stability and high temperature stability. However, the high prices for pure lanthanide materials are prohibitive for a more widespread commercialization. Furthermore, the pure mixed oxides typically used may be very refractory and very difficult to sinter into dense ceramic components.

(d) DESCRIPTION OF THE INVENTION

Broad aspects of this invention provide a novel lanthanide-based, complex oxide having an electrical conductivity at a high temperature, wherein a portion of the metal La in the general chemical formula is replaced by the metals Ce, Pr and Nd in amounts above 1%. This new material makes it possible to use partly-refined lanthanum raw material, often named "lanthanum concentrates" instead of more expensive, highly refined lanthanum chemicals. The presence of the other lanthanides in the complex mixed oxide, in addition to traces of other impurities originating from the partly-refined lanthanum raw material, enhances the sinter activity of the mixed oxide, making densification easier. Furthermore, the lanthanum deficiency in the mixed oxide induced by partly or completely replacing lanthanum with other lanthanides reduces the

detrimental reaction between lanthanum and other components adjacent to the mixed oxide material. This is a well known problem when using pure lanthanum ceramic materials as cell material in solid oxide fuel cells.

By a first broad aspect of this invention, a lanthanide oxide ceramic is provided having the general Formula $La_aLn_bM'_cM''_dO_{3-\delta}$, wherein Ln is a combination of Ce, Pr and Nd; M′ is at least one alkaline earth metal; M″ is at least one metal selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr; $0 \leq a \leq 1$; $0.01 < b \leq 1$; $0 \leq c \leq 0.6$; $0 \leq d \leq 1$; and $-1 < \delta < +1$. By a first variant thereof, the lanthanum oxide ceramic material has the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}MnO_3$. By a second variant thereof, the lanthanide oxide ceramic material has the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}CrO_3$.

In accordance with a second broad aspect of the present invention, an improvement is provided in a process of preparing a lanthanide oxide ceramic material which includes combining a source of lanthanide elements, a source of an alkaline earth metal, and a source of a metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr, and forming the ceramic material from the sources, the improvement which comprises: employing lanthanum concentrate as the source of the lanthanide elements, the lanthanum concentrate containing 40% LaO_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Nd_2O_3. By a first variant thereof, the source of lanthanide elements contain 0.01 atomic percent to 50 atomic percent of each of Ce, Pr and Nd, based on the total amount of lanthanide elements. By a second variant thereof the lanthanide oxide ceramic material is formed from a lanthanum concentrate containing 40% LaO_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Nd_2O_3, an alkaline earth metal, and a metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pr, Pt, Mg, Ru, Rh, Cr and Zr. By a first variation of that second variant thereof, the lanthanide oxide ceramic material which is formed from a lanthanum concentrate containing 0.01 atomic percent to 50 atomic percent of each of Ce, Pr, and Nd, based upon the total amount of lanthanide elements.

By a third aspect of this invention, an improvement is provided in a fuel cell having a ceramic material therein, wherein the ceramic material comprising a lanthanide

oxide ceramic material having the general formula $La_aLn_bM'cM''dO_{3-\delta}$, wherein Ln is a combination of Ce, Pr and Nd, M′ is at least one alkaline earth metal, M″ is at least one metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr; $0 \leq a \leq 1$; $0.01 < b\ 1$, $0 \leq c \leq 0.6$; $0 \leq d \leq 1$; and $-1 < \delta < +1$.

By a first variant of this third aspect of the invention, the ceramic material comprises a lanthanide oxide ceramic material which has the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}MnO_3$. By a second variant of this third aspect of the invention, the ceramic material comprises a lanthanide oxide ceramic material, which has the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}CrO_3$.

By a third variant of this third aspect of this invention, the improved fuel cell includes a ceramic material which is a lanthanide oxide material which is prepared by a first procedure as described hereinabove and which is formed from a lanthanum concentrate containing 40% LaO_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Na_2O_3, an alkaline earth metal, and a metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pr, Pt, Mg, Ru, Rh, Cr and Zr. By a fourth variant of this third aspect of the invention, the ceramic material comprises a lanthanide oxide ceramic material which is formed according to a second procedure as described hereinabove.

Changes in properties introduced by the other lanthanide elements when compared with mixed oxides without these other lanthanides may be compensated for by doping with other elements. For instance, in the case of lanthanum-based perovskites, the A-site may be doped with alkaline earth elements, e.g., Mg, Ca, Sr or Ba, and the B-site may be doped with metal elements or transition elements.

The lanthanide oxide ceramic material, according to an aspect of this invention, may be synthesized by mixing the partly-refined mixed lanthanide raw powder with strontium carbonate and manganese oxide, followed by calcination.

Another synthesis process, according to another aspect of this invention, is to dissolve the partly-refined mixed lanthanide raw powder in an acid, e.g., nitric acid, followed by the addition of salt solutions of strontium and manganese. This mixed salt solution may be pyrolysed to produce the desired lanthanide based material.

Lanthanum chromites represent state-of-the-art materials for use as current interconnections in SOFC's. This material has an ABO_3-type perovskite structure and alkaline earth metal cations (e.g., Mg, Ca, Sr or Ba) are often substituted for a fraction of La on the A-lattice site, thereby greatly enhancing the electrical conductivity. Lanthanum strontium chromites have become quite popular for SOFC interconnections due to an excellent combination of properties.

According to aspects of this invention, lanthanide ceramic materials may be prepared as described above and in the following examples.

(e) AT LEAST ONE MODE FOR CARRYING OUT THE INVENTION

Example 1

Commercial Lanthanum Concentrate containing 40% La_2O_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Nd_2O_3 plus 1% other lanthanides is dissolved in 65% HNO_3. This solution is combined with a 1 M solution of $Sr(NO_3)_2$ and $Mn(NO_3)_3$ in quantities according to the chemical formula:

$$La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}MnO_3$$

The resulting mixed salt solution is added glucose in a molar ratio of 1:1 with respect to the total metal cation

content and pyrolysed in a 600°C hot rotary furnace resulting in a single phase complex perovskite powder. After calcination at 900°C followed by ball milling the powder is suitable for traditional ceramic processing e.g. tape casting, screen printing or dry pressing. The X-ray diffraction spectrum of the calcined powder shows the characteristic lines for a single phase perovskite material.

Example 2

Commercial Lanthanum Concentrate containing 40% La_2O_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Nd_2O_3 plus 1% other lanthanides is mixed with $Sr(CO_3)_2$ and Cr_2O_3 in amounts according to the chemical formula:

$$La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}CrO_3$$

The powder mixture is calcined at 900°C followed by spray-drying. The spray-dried powder is shaped by dry pressing followed by sintering in air, argon or nitrogen at temperatures between 1400°C and 1700°C. The X-ray diffraction spectrum of the calcined powder shows the characteristic lines for a single phase perovsite material.

CLAIMS

1. A lanthanide oxide ceramic material having the general formula:

$La_aLn_bM'_cM''_dO_{3-\delta}$,

wherein

Ln is a combination of Ce, Pr and Nd;

M′ is at least one alkaline earth metal;

M″ is at least one metal selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr;

$0 < a \leq 1$;

$0.01 < b \leq 1$;

$0 \leq c \leq 0.6$;

$0 \leq d \leq 1$; and

$-1 < \delta < +1$.

2. The lanthanide oxide ceramic material as claimed in claim 1, having the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}MnO_3$.

3. The lanthanide oxide ceramic material as claimed in claim 1, having the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}CrO_3$.

4. An improvement in a process of preparing a lanthanide oxide ceramic material which includes combining a source of lanthanide elements, a source of an alkaline earth metal, and a source of a metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr, and forming the ceramic material from said sources, the improvement which comprises: employing lanthanum concentrate as the source of the lanthanide elements, said lanthanum concentrate containing 40% LaO_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Nd_2O_3.

5. The improvement as claimed in claim 4, wherein the source of lanthanide elements contain 0.01 atomic percent to 50 atomic percent of each of Ce, Pr and Nd, based on the total amount of lanthanide elements.

6. The improvement as claimed in claim 4, wherein the lanthanide oxide ceramic material comprises the material as claimed in claim 3, which is formed from a lanthanum concentrate containing 40% LaO_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Nd_2O_3, an alkaline earth metal, and a metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pr, Pt, Mg, Ru, Rh, Cr and Zr.

7. The lanthanide oxide ceramic material as claimed in claim 6, which is formed from a lanthanum concentrate containing 0.01 atomic percent to 50 atomic percent of each of Ce, Pr, and Nd, based upon the total amount of lanthanide elements.

8. In a fuel cell having a ceramic material therein, the improvement which comprises providing, as said ceramic material, a ceramic material comprising a lanthanide oxide ceramic material having the general formula of:

$$La_aLn_bM'_cM''_dO_{3-\delta},$$

wherein

Ln is a combination of Ce, Pr and Nd;

M′ is at least one alkaline earth metal;

M″ is at least one metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pd, Pt, Mg, Ru, Rh, Cr and Zr; and

$0 < a \leq 1$;

$0.01 < b \leq 1$;

$0 \leq c \leq 0.6$;

$0 \leq d \leq 1$; and

$-1 < \delta < +1$.

9. In a fuel cell having a ceramic material therein as claimed in claim 8, the improvement which comprises providing, as said ceramic material, a ceramic material comprising a lanthanide oxide ceramic material, having the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0.15}MnO_3$.

10. In a fuel cell having a ceramic material therein, as claimed in claim 8, the improvement which comprises providing, as said ceramic material, a ceramic material comprising a lanthanide oxide ceramic material, having the formula $La_{0.54}Ce_{0.05}Pr_{0.07}Nd_{0.18}Sr_{0\ 15}CrO_3$.

11. In a fuel cell having a ceramic material therein, as claimed in claim 8, the improvement which comprises providing, as said ceramic material, a ceramic material comprising the lanthanide oxide ceramic material as claimed in claim 6, which is formed from a lanthanum concentrate containing 40% LaO_3, 4% CeO_2, 5.5% Pr_6O_{11} and 13.5% Nd_2O_3, an alkaline earth metal, and a metal which is selected from the group consisting of Co, Fe, Ni, Zn, Cu, Mn, Al, V, Ir, Mo, W, Pr, Pt, Mg, Ru, Rh, Cr and Zr.

12. In a fuel cell having a ceramic material therein, as claimed in claim 8, the improvement which comprises providing, as said ceramic material, a ceramic material comprising a lanthanide oxide ceramic material which is formed according to the improvement as claimed in claim 5.