PROTON-CONDUCTIVE ELECTROLYTE MATERIALS FOR PROTONIC CERAMIC FUEL CELLS (PCFCs)

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ABSTRACT

Two groups of proton conducting ceramic materials have been synthesized. The first one consisted of stoichiometric ACe0.85M0.15O3-δ, where A is Ba and M is Ga or In. The second group included yttrium doped barium zirconates of the general formula BaZr1-xYxO3-δ where x=0.025, 0.05, 0.075, 0.1, 0.15, and 0.2, and δ=x/2. Gallium and indium doped alkali earth metal cerates were processed using glycine nitrate methods, followed by a variation on the Pechini synthesis process. X-ray diffraction spectra of these materials agrees with existing spectra in the ADAMA database. SEM images were made for both groups, revealing a dense ceramic structure for BaCe0.85In0.15O3-δ and non-uniform grain sizes for BaCe0.85Ga0.15O3-δ. SEM images for the yttrium doped barium zirconates reveal a structure more porous than that of the barium cerates. X-ray diffraction spectra of the yttrium doped barium zirconate material also agrees with existing spectra from the database.

INTRODUCTION

Intermediate temperature dense ceramic membranes with mixed hydrogen ionic and electronic conductivity are receiving considerable attention (1,2,3,4) due to their potential applications in fuel cells, steam electrolyzers, hydrogen sensors, fossil fuel plants, and hydrogen separation membranes and modules. In contrast to SOFCs (5) with oxygen ion conducting electrolytes, PCFCs (6) form water at the cathode thus leaving pure fuel at the anode without additional recirculation. Furthermore, the thermodynamic efficiency of PCFCs is the highest available among all types of fuel cells.

Among different groups of organic and inorganic materials (7,8), the proton conductive perovskite-type oxides are the most promising candidates for hydrogen separation membranes since their conductivity, when measured below 250°C and extrapolated to higher temperatures, is comparable to that of the best oxygen ion-conductors. These materials, if used in PCFC, are targeted for operation at 55-65% electrical efficiency on pipeline natural gas, which is impossible for any other kind of fuel cell. Moreover, in the perovskite-type oxides a variety of elements can be accommodated within the crystal lattice, and aliovalent cations can be doped relatively easily to form ion vacancies. According to available theoretical assumptions and experimental data, the presence of...
oxygen vacant sites in the perovskite ceramic material is essential for hydrogen ion transport and proton conductivity.

Among perovskite type oxides, the highest protonic conductivities have been obtained for barium cerates doped with La$^{3+}$ and Y$^{3+}$ for Ba$^{2+}$ and Ce$^{4+}$ at 700°C with $\sigma$=29 mS/cm in dry oxygen and $\sigma$=20 mS/cm in wet hydrogen. However, these barium cerates showed poor stability in carbon dioxide – containing atmospheres due to the formation of BaCO$_3$ (9). Moreover, evaporation of BaO shown for cerates (10,11), revealed the presence of ZrO$_2$ phase at the surface (12) in BaZr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ system.

Increasing the dopant concentration in perovskite phases of the general formula $\text{AB}_{1-x}\text{B}_x\text{O}_{3-\delta}$ leads to higher oxygen vacancy concentration and higher proton conductivity (13); however inhibiting grain growth, decreasing densities and purity of the phases (14,15). Possible alternatives could be to decrease the membrane thickness, while maintaining a low dopant concentration.

The objective of this work was to synthesize proton conductive alkaline earth metal cerates doped with indium and gallium and to provide x-ray diffraction spectra and SEM images. Barium zirconates, synthesized by Ceramem Corp., were also analyzed using x-ray diffraction spectra, as well as SEM spectroscopy.

**EXPERIMENTAL**

The first group of synthesized materials included stoichiometric gallium and indium-doped alkaline-earth metal cerates $\text{ACe}_{0.85}\text{Mo}_{1.15}\text{O}_{3-\delta}$, where A is Ba and M is Ga or In. The second group comprised yttrium doped barium zirconates of the general formula $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-\delta}$, where $x=0.025$, 0.05, 0.075, 0.1, 0.15, and 0.2, and $\delta=x/2$. The values of $x$ were chosen to represent the range over which doping has the most effect on increasing the defect concentration (being 0-20%) of dopant without adversely affecting the overall stoichiometry, i.e., causing any second phase development by exceeding the upper limit of solid solution formation.

Gallium and indium doped alkali earth metal ceramics were processed using glycine nitrate methods (16). In this method, glycine, which prevents precipitation in the precursor solution and acts as the oxidizer, was dissolved in water and mixed with corresponding 99.99% pure nitrate salts from Alfa Aesar (Johnson Matthey Company) in a stoichiometric ratio. The exact composition of the $\text{Ce(NO}_3)_3 \times \text{H}_2\text{O}$ precursor was determined in 0.1 M solution of cerium nitrate via atomic adsorption spectroscopy using a Perkin Elmer 3300 analyzer. All precursors were homogeneously distributed at the molecular level in solution, which then had been heated at 90°C in a high vacuum oven to evaporate water. The glassy compositions obtained were heated at 300°C with further ignition in a modified Pechini synthesis process, yielding a voluminous, black porous ash, which was subsequently ground in a mortar and pestle. The material was sintered in a Carbolite high temperature furnace at 1500°C for five hours, with a 5°/min ramp on heating and cooling. This material was studied using x-ray diffraction. Upon completion, the material was used to create two pellets of each material (BaCeIn and BaCeGa) and placed back in the furnace for another sintering process at 1500°C for
sixteen hours, with a 5°/min ramp on heating and cooling. This last step was repeated once, for a total of three separate sintering processes. SEM images were made along each step in the process.

In parallel, pure Ba, Ce, Ga, and In oxides were also synthesized and sintered at 800°C and 1400°C for 5 hours with a 5°/min ramp on heating and cooling. Yttrium doped barium zirconates were synthesized using classical solid-state reaction methods at Ceramem Inc. The material was analysed using x-ray diffraction methods as well as SEM.

X-ray powder diffraction was performed at room temperature on a theta-theta Bruker-AXS D5005 reflection diffractometer equipped with 2.2 KW Cu X-ray tube and a Goebel mirror-parallel beam optical system. Unit cell dimensions were determined by the least squares method included in the Visual-Xpow Stoe software, which allowed for adjustment of a zero-shift in 2-theta (typically below 0.02 degrees).

Density measurements of the sintered samples were obtained using the standard Archimedes technique. In this method, the weight of a pelletized specimen is recorded before and after being boiled in distilled water. The pellet is then suspended in water and re-weighed. The bulk density $B$ is calculated using equation 1:

$$B = \frac{W_d - W_s}{W_w - W_s}$$  \[1\]

where $W_d$ is the weight of the dry sample, $W_w$ is the weight of the wet sample, and $W_s$ is the weight of sample suspended in water.

The theoretical density $T_d$ is calculated using the equation:

$$T_d = \frac{Z M_C V_C N_A}{V_c}$$  \[2\]

where $Z$ is the number of chemical species in the unit cell, $M_C$ is the molar mass of a single chemical species corresponding to the chemical formula (g/mol$^-$), $V_c$ is the unit cell volume ($\text{Å}^3$), and $N_A$ is Avogadro’s number (6.0221x$10^{23}$ mol$^{-1}$). The cell parameters are calculated using orthorhombic symmetry and $Z=4$. Theoretical densities are estimated from XRD patterns using $d$ spacing and a UNITCELL program parameter calculation. Unit cell dimensions were determined by the least squares method included in the Visual-Xpow Stoe software, which allows for adjustment of a zero-shift in 2-theta (typically below 0.02 degrees). The percentage theoretical density ($\% \rho$) was calculated using equation:

$$\% \rho = \frac{B}{T_d} \times 100\%$$  \[3\]

RESULTS AND DISCUSSION

**X-ray Diffraction Spectra**

This part of the work represents our preliminary x-ray diffraction data related to the synthesis of In and Ga doped-alkali earth metal cerates, as well as that of the barium zirconates. Figure 1 presents the x-ray diffraction spectra of $\text{BaCe}_{0.85}\text{In}_{0.15}\text{O}_3\alpha$, $\text{BaCe}_{0.85}\text{In}_{0.15}\text{O}_3\beta$, $\text{BaCe}_{0.85}\text{In}_{0.15}\text{O}_3\gamma$, and $\text{BaCe}_{0.85}\text{In}_{0.15}\text{O}_3\delta$. These spectra show the characteristic peaks of the different phases, which are used to identify the crystal structure and purity of the synthesized materials.
BaCe$_{0.85}$Ga$_{0.15}$O$_3$-$\alpha$, and BaZr$_{1-x}$Y$_x$O$_{3-\delta}$. All three are in accordance to materials spectra found in the ADAMA database.

Cerium oxide, as a fluorite-structured ceramic material, does not show any known crystallographic change from room temperature up to its melting point (17). Doping with aliovalent alkaline-earth cations, such as barium, introduce oxygen vacancies in its structure for charge compensation and make these systems relevant as proton conductors at elevated temperatures in the presence of water vapor.

Table I represents data unit cell volumes calculated from x-ray diffraction and corresponding crystal structures. The CeO$_2$ sample sintered at 800°C (Figure 2) has exhibited nearly all the characteristic reflections corresponding to the fluorite-structured CeO$_2$. The same characteristic reflections were identified in x-ray diffraction spectra after the ignition process (300°C) and at higher sintering temperature (1400°C). With increase in sintering temperature the peaks grow narrower and sharper, indicating crystallite growth. The x-ray diffraction patterns of other pure oxides, except Ga$_2$O$_3$, were in almost
perfect correlation with existing files from the x-ray diffraction database and were used for the estimation of possible trace amounts of corresponding oxide phases in perovskite materials.

Table I. Unit Cell Volumes.

| Oxides   | Crystal Structure     | Unit Cell Volume, Å³ | Ref. from JCPDF database |
|----------|-----------------------|----------------------|--------------------------|
| BaO      | Body-Centered Tetragonal | 99.87                | 7-223                    |
| CeO₂     | Face-Centered Cubic   | 162.26               | 34-394                   |
| Ga₂O₃    | Rhombohedral          | 288.80               | 43-1013                  |
| In₂O₃    | Body-Centered Cubic   | 1051.43              | 6-416                    |

Figure 2 presents the x-ray diffraction spectra of Ba, Ce, Ga, and In oxides sintered at 800°C and 1400°C for 5 hours for comparison with diffraction spectra from Figure 1.

![Figure 2. X-ray diffraction spectra of Ba, Ce, Ga, and In oxides.](image-url)

It was difficult to determine the presence of cerium oxide phase in the synthesized samples due to the fact that many of the diffraction peaks could overlap with those of indium or gallium doped alkaline-earth metal cerates (10). However, comparison of the
spectra with the data available in literature indicates that the synthesized structures belong to perovskite proton conducting ceramic oxides.

SEM images of BaCe$_{0.85}$Ga$_{0.15}$O$_{3}$-a and BaZr$_{1-x}$Y$_x$O$_{3}$-8 are presented in Figure 3.

![SEM images](image)

**Figure 3.** BaCe$_{0.85}$In$_{0.15}$O$_{3}$-a viewed at 10 μm (a) and at 50 μm (b) looks more dense than BaZr$_{0.85}$Y$_{0.15}$O$_{3}$-8 viewed at 10 μm (c). BaCe$_{0.85}$Ga$_{0.15}$O$_{3}$-a viewed at 10 μm (d) and at 50 μm (e) looks similar to the corresponding Indium images.

Theoretical density calculations using the X-ray data show a decrease in density with Y$_2$O$_3$ content, which may be attributed to a distortion of the unit cell. The requirements for ceramic electrolytes are met at a low dopant concentration at x=0.02 and x=0.05, and at x=0.2 where the relative density is in the range 97%-99%. In the range from x=0.15 to x=0.075, the relative density is less than 95%, which does not meet the necessary requirements of only having closed porosity.
CONCLUSIONS

Proton-conductive electrolyte materials of the general structure ACe$_{0.95}$M$_{0.05}$O$_{3-\delta}$, where A = Ca, Sr, Ba and M = Ga and In were synthesized using nitrate glycine sol-gel method; however additional efforts should be made for detailed evaluation of crystal structure of these oxides. These oxides will be also used for the estimation of their mechanical and electrical properties. Yttrium doped strontium cerates were synthesized via a solid-state reaction method. Changing the yttrium content in SrCe$_{1-x}$Y$_x$O$_{3-\delta}$, where x=0.025, 0.05, 0.075, 0.1, 0.15, and 0.2, and $\delta=x/2$, affects the electrical and structural properties of the system. Unit cell volume and calculated density decrease with increasing yttrium content.

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