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Enhanced Ionic Conductivity in an Otherwise Poorly Conducting $Ce_{0.90}Ca_{0.10}O_{2-\delta}$ System

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A poorly conducting ionic material $Ce_{0.90}Ca_{0.10}O_{2-\delta}$ was converted to a highly conducting composition by a codoping strategy with Sm^{3+} and Gd^{3+}. A 50% replacement of Ca with either Sm or Gd has increased the conductivity at 550 °C of $Ce_{0.90}Ca_{0.10}O_{2-\delta}$ from 0.0040 to 0.0169 S/cm for the $Ce_{0.90}Ca_{0.05}Sm_{0.05}O_{2-\delta}$ composition and to 0.0184 S/cm for the $Ce_{0.90}Ca_{0.05}Gd_{0.05}O_{2-\delta}$ composition. The enhancement in the oxide ion conductivity of these codoped samples has been related to the low ionic radii mismatch and the elastic strain. The extended X-ray absorption fine structure measurements on these systems confirmed that Gd, when coupled with Ca, introduced more disorder in the system, leading to lower activation energy and higher conductivity. In addition, a reduction in the Ce−O bond distance and coordination number has also been observed with codoping.

In order to extend the application domain of solid oxide fuel cell (SOFC) technology to portable power sectors, the operating temperature of the cells should be reduced. Solid electrolytes with high ionic conductivity at lower temperatures are the key materials for such applications. Gd- and Sm-doped ceria are considered to be the most promising low-temperature solid electrolytes for such applications because of their higher oxide ion conductivity at lower temperatures (500−700 °C).[1] However, from the viewpoint of material expenses, both Gd and Sm are very costly. In order to improve the cost effectiveness and properties of the existing materials and to identify newer compositions with enhanced properties, a codoping strategy has been introduced.[2−5] New systems explored in this strategy include $Ce_{1-x-y}Gd_xPr_yO_{2-\delta}$, $Ce_{1-x-y}Sm_xLa_yO_{2-\delta}$, $Ce_{1-x-y}Y_xLa_yO_{2-\delta}$, and $Ce_{1-x-y}Gd_x$-$Sm_yO_{2-\delta}$, wherein improvement in the conductivity has been noticed.[6−13] Our recent studies on the $Ce_{1-x}Ca_xO_{2-\delta}$ samples revealed an enhanced sinterability by doping with Ca albeit they are poorly ionic conducting.[13] By considering the dual advantage of using Ca as a dopant because of its high sinterability and low cost, we have recently reported a new series of ion-conducting compounds by partially replacing Sm with Ca in $Ce_{0.8}Sm_{0.2}O_{1.9}$.[14] In this letter, the effect of codoping on the structure and ionic conductivity of a poorly conducting $Ce_{0.90}Ca_{0.10}O_{2-\delta}$ composition was investigated and evolved a newer composition with enhanced conductivity for IT SOFC applications.

A mixed fuel process was adopted to prepare nanocrystalline $Ce_{0.90}Ca_{0.05}M_{0.05}O_{2-\delta}$ (M = Gd, Sm) samples that could be sintered to nearly full density at 1200 °C.[13,14] Ammonium cerium(IV) nitrate (Merck Ltd., India), calcium nitrate (S.D. Fine Pvt. Ltd., India), and samarium nitrate and gadolinium nitrate (Aldrich) were used for the preparation of the samples. For convenience, the compositions $Ce_{0.90}Ca_{0.10}O_{2-\delta}$, $Ce_{0.90}Ca_{0.05}Sm_{0.05}O_{2-\delta}$, and $Ce_{0.90}Ca_{0.05}Gd_{0.05}O_{2-\delta}$ will be designated as CCO, CCS, and CCG, respectively.

Powder X-ray diffraction (XRD) was carried out on both the combustion-synthesized and calcined powders for phase identification. All the reflections of the undoped CeO_2 (JCPDS-34-394) were present in the XRD patterns of the doped samples, thereby confirming the ability of this synthetic approach in preparing doped nanoparticles at a low temperature. The calculated lattice parameters of CCO,

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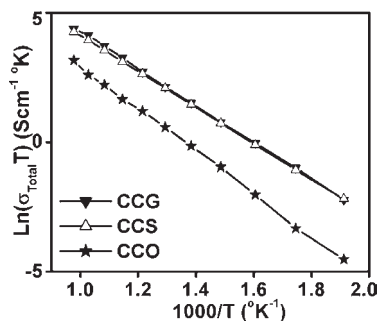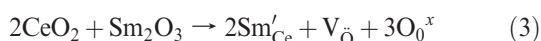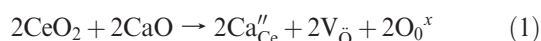
Figure 1. Arrhenius plots of the total conductivity of the investigated compositions.

CCS, and CCG are 5.425(3), 5.425(1), and 5.424(8) Å, respectively. Though the ionic radii of the dopant cations decrease in the order Ca^{2+} (1.12 Å) > Sm^{3+} (1.079 Å) > Gd^{3+} (1.053 Å) > Ce^{4+} (0.97 Å), a consequent change was not observed in the lattice parameter probably because of the low concentration of the codopant ions introduced. Sintering was performed in air at 1200 °C for the CCG and CCS samples and at 1250 °C for the CCO sample for 6 h with a heating rate of 10 °C/min. The relative density of the codoped CCS and CCG samples reached a maximum of around 96−97% at 1200 °C, which is substantially lower than the available reports for any of the codoped ceria compositions (1300−1600 °C).[3−14]

Two probe alternating-current impedance measurements were conducted on the sintered samples in the frequency range of 1 Hz to 10 MHz with an applied voltage of 0.1 V using a Solartron frequency response analyzer (FRA 1260) coupled with a Solartron 1296 dielectric interface unit in the temperature range 250−900 °C in air. In Figure 1, the Arrhenius plots of the total conductivity (σ_T) for all of the compositions are presented. The total oxide ion conductivity varied in the order $\sigma_{CCO} < \sigma_{CCS} < \sigma_{CCG}$. The total conductivity at 650 °C along with the activation energy calculated from the Arrhenius plots is given in Table 1. Both codoped compositions, CCS and CCG, exhibited higher oxide ion conductivity than the single-doped CCO analogue. A 50% replacement of Ca with either Sm or Gd has increased the conductivity of $Ce_{0.90}Ca_{0.10}O_{2−\delta}$ from 0.0040 to 0.0169 S/cm at 550 °C for the $Ce_{0.90}Ca_{0.05}Sm_{0.05}O_{2−\delta}$ composition and to 0.0184 S/cm for the $Ce_{0.90}Ca_{0.05}Gd_{0.05}O_{2−\delta}$ composition. Among the compositions investigated, a maximum conductivity with a minimum activation energy was achieved for the Ca- and Gd-codoped composition $Ce_{0.90}Ca_{0.05}Gd_{0.05}O_{2−\delta}$ ($\sigma_{650 °C} = 0.045$ S/cm; $E_a = 0.67$ eV), which is, in fact, much higher compared to the reported values for Gd-, Sm-, or Gd−Sm-codoped ceria samples.[1−12]

In general, a system having a highly symmetric and stable structure containing more oxygen vacancies is expected to exhibit high oxide ion conductivity. The following equations clearly show that the incorporation of divalent Ca^{2+} into the CeO_2 lattice introduces more oxygen vacancies than the incorporation of trivalent ions Gd^{3+} or Sm^{3+}.

$$2CeO_2 + 2CaO \rightarrow 2Ca''_{Ce} + 2V_{\ddot{O}} + 2O_0^x \qquad (1)$$

$$2CeO_2 + Gd_2O_3 \rightarrow 2Gd'_{Ce} + V_{\ddot{O}} + 3O_0^x \qquad (2)$$

$$2CeO_2 + Sm_2O_3 \rightarrow 2Sm'_{Ce} + V_{\ddot{O}} + 3O_0^x \qquad (3)$$

The oxygen vacancy calculated for each composition based on the electroneutrality condition is shown in Table 1. It is evident from Table 1 that the level of oxygen vacancies (δ) varies in the order $\delta_{CCG} = \delta_{CCS} < \delta_{CCO}$, and consequently the CCO sample is expected to exhibit the highest conductivity if the oxygen vacancy is the only deciding factor in exhibiting the ionic conductivity. However, our measurements show that the conductivity varied in the order $\sigma_{CCO} < \sigma_{CCS} < \sigma_{CCG}$, with CCO having the lowest conductivity. This observation implies that the presence of a high concentration of oxygen vacancies is not the main criteria for obtaining high ionic conductivity. The underlying question to be answered here is the role of Gd or Sm as a codopant with Ca and their influence on the structural stability of ceria. To find an answer to this question, we first calculated the ionic radii mismatch, taking into consideration the ionic radii of the host and the dopant cations as shown in Table 1. Here, r_d is the average ionic radius of the dopant cations and r_h is the ionic radius of the host cation Ce^{4+}, which is 0.97 Å. Kilner discussed the effect of different dopants on the ionic conductivity of the fluorite-type MO_2 oxides based on the ionic radii mismatch and concluded that a minimum value of $r_d − r_h$ maximizes the oxide ionic conductivity.[15] From the data shown in Table 1, it is clear that the lattice mismatch is lowest when doped with Gd^{3+} compared to Sm or Ca. Because $r_{Gd^{3+}} = 1.053$ Å is lower than $r_{Sm^{3+}} = 1.079$ Å, the ionic radii mismatch ($r_d − r_{Ce^{4+}}$) is lower for CCG than for CCS and, consequently, the former shows a slightly higher conductivity than the latter, in spite of having similar δ values. In addition to this radii mismatch, the elastic strain,[3] which is a direct measure of the strain created in the doped lattice, was also calculated as elastic strain $= (a − a_0)/a_0$, where a is the lattice parameter of the doped system and a_0 that of the undoped composition. As could be seen from Table 1, CCG introduces less strain compared to CCS.

At 650 °C, the single-doped $Ce_{0.90}Ca_{0.10}O_{2−\delta}$, $Ce_{0.90}Sm_{0.10}O_{2−\delta}$, and $Ce_{0.90}Gd_{0.10}O_{2−\delta}$ samples exhibited conductivities of 0.0100, 0.0285, and 0.0357 S/cm, respectively, whereas the codoped samples $Ce_{0.90}Ca_{0.05}Gd_{0.05}O_{2−\delta}$ and $Ce_{0.90}Ca_{0.05}Sm_{0.05}O_{2−\delta}$ exhibited much higher conductivities of 0.0450 and 0.0378 S/cm, respectively. It is interesting that a mixture of divalent and trivalent cations has resulted in lower ionic radii mismatch and elastic strain, thus giving rise to compositions exhibiting higher ionic conductivity than either of the individual ions. Thus, the introduction of the trivalent dopants Gd and Sm as codopants in $Ce_{0.90}Ca_{0.10}O_{2−\delta}$ has resulted in a series of cost-effective codoped $Ce_{0.90}Ca_{0.05}Gd_{0.05}O_{2−\delta}$ and $Ce_{0.90}Ca_{0.05}Sm_{0.05}O_{2−\delta}$ ceria compositions with high conductivities in the low-temperature region for technological applications..

In order to find out the valence state and the local structure of cerium in these newly prepared codoped compositions, X-ray absorption fine structure (EXAFS) measurements were carried out at the Ce L_3 edges in transmission mode at the EXAFS-1 Beamline at the Elettra Synchrotron Source using Si(111) as the monochromator. Data analysis was carried out using *IFEFFIT* in *ATHENA* and *ARTEMIS* programs.[16−18] The data in the k range of 2−12 Å^{-1} were used for analysis.

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Table 1. Ionic Conductivity and Related Data of the Codoped Compositions

sample	δ value	r_d (Å)	$r_d - r_{Ce^{4+}}$ (Å)	elastic strain $(a - a_0)/a_0$ (± 0.0001)	$\sigma_{650\,°C}$ (S/cm)	E_a (eV)
CCO	0.10	1.120	0.150	0.0027	0.0100	0.76
CCS	0.075	1.0995	0.1295	0.0026	0.0378	0.68
CCG	0.075	1.0865	0.117	0.0025	0.0450	0.67
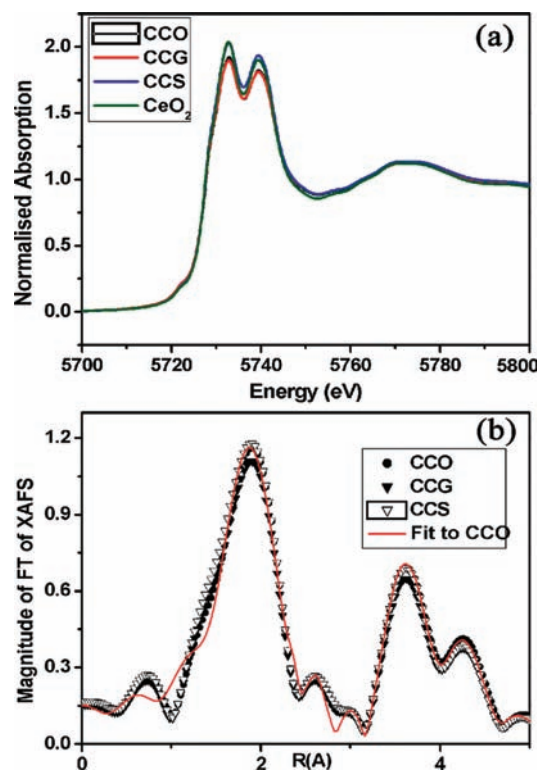
Figure 2. (a) Normalized Ce L$_3$-edge XANES spectra of CCO, CCS, and CCG and pure CeO$_2$ and (b) Fourier transform magnitude of the L$_3$-edge XANES (color online).

X-ray absorption near-edge spectra (XANES) of all three samples are shown in Figure 2a. No changes in the edge position or edge features were seen in comparison to pure CeO$_2$ (Figure 2a). This clearly indicates that, in all of the doped compounds, Ce is present in the tetravalent (4+) state only. The magnitude of the Fourier transform of Ce L$_3$ EXAFS is presented as a radial structure function (RSF) in Figure 2b. The two peaks corresponding to the interatomic distances of Ce−O (first shell) and Ce−Ce (second shell) are clearly evident in the RSF figure. The first peak centered at about 2 Å is the Ce−O correlation, while the double-peak structure in the 3−4.5 Å range is due to scattering from atoms in the higher coordination shells. The experimental data were fitted to a model based on the CeO$_2$-type fluorite structure. Inclusion of dopant Ca, Gd, or Sm did not have any significant effect on the fitting, and hence only Ce−O and Ce−Ce correlations are reported in Table 2. A reduction in the EXAFS amplitude of Ce−O is evident in Figure 2b, which is an indication of a reduction in the coordination number. The smaller amplitude of the second shell corresponding to the Ce cation is due to the high degree of structural disorder caused by the introduction of a second dopant into the ceria lattice.

Table 2. Structural Features Based on the EXAFS Studies Conducted on the Doped Samples

bond type	bond distance (Å)	MSRD (Å^2)	coordination number
	$Ce_{0.9}Ca_{0.05}Gd_{0.05}O_{2-\delta}$		
Ce−O	2.322(5)	0.009(1)	7.2(4)
Ce−Ce	3.863(5)	0.005(1)	12
	$Ce_{0.9}Ca_{0.05}Sm_{0.05}O_{2-\delta}$		
Ce−O	2.321(6)	0.009(1)	7.4(4)
Ce−Ce	3.859(7)	0.005(1)	12
	$Ce_{0.95}Ca_{0.05}O_{2-\delta}$		
Ce−O	2.326(5)	0.010(1)	7.5(3)
Ce−Ce	3.877(5)	0.005(1)	12

More disorder is seen for the Gd-codoped CCG sample than the CCS sample. In the case of pure CeO$_2$, the Ce−O bond distance is about 2.33 Å while the Ce−Ce correlation appears at 3.87 Å. In the case of doped compounds, the bond distance Ce−O and Ce−Ce varied in the order CCO > CSO > CGO. Taking into consideration the small amount of the dopant that has been added to the ceria system, one cannot expect a significant change in the bond length. Hence, we noticed only a marginal change, as is evident from the data shown in Table 2. The coordination number also shows a decrease from 8 for pure CeO$_2$ to 7.2(4) for the CCG sample, and it varied in the order CCO > CCS > CCG. Here, again, the coordination number is lowest for the Gd-containing sample. Therefore, from the EXAFS data, it can be concluded that when Ca is coupled with Gd, the CaGd combination introduces more disorder into the system, thereby giving rise to a higher conductivity and lower activation energy.

In conclusion, we report here a new series of oxide ion conducting materials in the $Ce_{0.90}Ca_{0.10}O_{2-\delta}$ system with enhanced conductivity by codoping with Gd and Sm. Moreover, the codoping has also improved the sintering characteristics of the host composition, and at 1200 °C, samples with density > 97% of the theoretical densities were produced. The highest conductivity was exhibited by the Ca- and Gd-codoped ceria sample ($\sigma_{650\,°C} = 0.045$ S/cm; $E_a = 0.67$ eV). XANES studies confirmed the presence of only Ce^{4+} in these systems. Our experimental results, thus, suggest that the choice of dopants is highly critical and plays a vital role in controlling the properties of the codoped samples.