Complementary Effect on the Total Conductivity: Addition of Sr^{2+} in Ta^{5+} Doped Ceria

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Abstract: Sr^{2+} and Ta^{5+} co-doped samples were prepared by solid state doping and investigated in order to see the commutation effect on total conductivity by addition of acceptor dopant (Sr^{2+}) in presence of donor dopant (Ta^{5+}) in ceria sample. X-ray diffraction proved that both of the dopants were completely soluble in ceria and the resultant composition was the single phase oxide solid solution having fluorite structure. Total conductivity and activation energy with the help of impedance measurements are calculated. Theoretical assumptions with the help of electro neutrality relation showed that the required amount of Sr^{2+} to fully neutralize the effect of Ta^{5+} should be nearly half of the amount of Ta^{5+} (i.e. 1.5% Sr^{2+} for 3% Ta^{5+}). Whereas experimental results show the maximum total conductivity for 3% Ta doped ceria and as the amount of Sr is increased in the sample, it decreases. The minimum in total conductivity appears for the composition having 4% Sr^{2+} + 3% Ta^{5+} doping which results a contradiction with the theoretical approach. Further increase in the amount of Sr^{2+} again increases the total conductivity.

Keywords: Total conductivity, Doped ceria, Impedance spectroscopy.

1. Introduction

Among solid ionic conductors, oxygen ion conductors play a key role. Their use in SOFCs and exhaust gas sensors is well known [1, 2]. Doped ceria has been investigated for long time, although its envisaged application in low temperature SOFCs as electrolyte has not been realized on a larger scale [3-5]. Instead, undoped ceria as well as solid solutions of ceria and zirconia are becoming increasingly important due to their fast, reversible oxygen storage properties which lead to their use as active additives in exhaust gas and water gas shift catalysts [6]. Fast reversible oxygen incorporation and the ability for fast electron exchange under low oxygen partial pressures were also the reasons why ceria now is widely used as anode additive in SOFC [1]. This multipurpose nature as good oxygen ion conductor and fast electron exchange material coincides with an extraordinary chemical and thermal stability from room temperature up to at least 1000 °C and a considerable tolerance for reducing atmospheres without phase change [7, 8]. Some recent studies even point out that doped ceria may be used in oxygen permeation membranes [9, 10].

Ceria based solid oxide solutions can readily be used in various components in SOFC. SOFCs are usually operated at high temperature near 1000 °C which in turn introduce numerous problems due to the chemical instability of electrodes, sealing glass, interconnects etc. [11]. To optimize these difficulties, it is necessary to introduce the electrolyte and anode materials with comparatively smaller ohmic losses which require good ionic and electronic conductivity with ability to withstand such high temperatures. Various acceptor ions (e.g. Y, Yb, Gd, Sr etc.) doped Ceria have been reported to result in good ionic conductivity [12, 13] and therefore, are good candidates to be used as an efficient solid electrolyte at intermediate temperatures around 700 °C [14]. Some donor ions (e.g. Ta, Nb etc) doped ceria materials have been investigated for their electronic conductivities [15]. Ta doped ceria and Sr doped ceria are found to be as

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good electronic and good ionic conductor respectively. In present work, we investigated total conductivity with changing amount of acceptor dopant in donor doped ceria.

2. Theoretical consideration

Pure ceria, i.e. CeO$_2$, crystallizes in the fluorite structure. The Ce^{4+} ions form a FCC structure where half of the tetrahedral voids are occupied by oxide ions. Nominally pure ceria exhibits a weak electronic conductivity which is due to an effective band gap of about 3.2 eV corresponding to the distance between valence band maximum and Ce4f levels. Depending on the stoichiometric composition, n-type conduction occurs under reducing atmospheres. The electrons are highly localized on 4f levels of the cerium ions forming Ce^{3+} and, hence, are transported via a small polaron mechanism. The electron-hole pair formation equilibrium is given by[1],

$$K_{eh} = [\,e'\,] \cdot [\,h^\bullet\,] = K_{eh}^{\,\circ} \exp\left[-E_{gap}/kT\right] \tag{1}$$
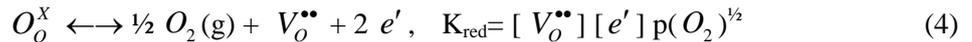
The intrinsic ionic defects are assumed to be Frenkel defects as is often found for compounds with fluorite structure. Oxygen vacancies are predominating in a wide range of oxygen partial pressures, their concentration can easily be enhanced by acceptor doping with lower valent cations such as Y^{3+}, Gd^{3+} etc. There is no clear prove for the existence of oxygen interstitials, although indications have been found at high oxygen partial pressures and for doping with donor ions such as Nb^{5+}. The Frenkel pair formation is described by the following equation:

$$K_F = [\,O_i''\,] \cdot [\,V_O^{\bullet\bullet}\,] = K_F^{\,\circ} \exp\left[-E_F/kT\right] \tag{2}$$

$V_O^{\bullet\bullet}, O_i'', e'$ and $h^\bullet$ denote an oxygen vacancy (two positive charges), an oxygen ion at interstitial site (two negative charges), an electron (corresponding to Ce^{3+}) and a hole with one positive charge, respectively. Rectangular brackets denote the corresponding concentrations. K_F and K_{eh} are the equilibrium constant for Frankel pair formation and electron hole formation in intrinsic ceria respectively. The good oxygen storage properties of nominally pure ceria suggest that K_F and K_{eh} both have non-negligible values at temperatures above 500 ℃ [16]. Thus, the defect concentrations in pure ceria must obey the following electro-neutrality condition (where we neglect any trapping of holes or electrons on the vacancies and interstitials, for the sake of simplicity)

$$0 = [\,h^\bullet\,] - 2\,[\,V_O^{\bullet\bullet}\,] - [\,e'\,] + 2\,[\,O_i''\,] \tag{3}$$

Changing the oxygen partial pressure of oxygen will lead to coupled changes of these defect concentrations due to the following equilibrium with the reduction equilibrium constant K_{red}

$$O_O^X \longleftrightarrow \tfrac{1}{2}\,O_2(g) + V_O^{\bullet\bullet} + 2\,e', \quad K_{red} = [\,V_O^{\bullet\bullet}\,]\,[\,e'\,]\,p(O_2)^{\frac{1}{2}} \tag{4}$$

As we want to investigate the role of co-doping by Ta^{5+}, acting as a positively charged substituent on Ce^{4+} sites (=donor dopant), and Sr^{2+} acting as substituent defect with two negative charges on Ce^{4+} sites (=acceptor dopant), the electro-neutrality (3) has to be enlarged to give

$$[Ta_{Ce}^\bullet] - 2[Sr_{Ce}''] = [\,h^\bullet\,] - 2[\,V_O^{\bullet\bullet}\,] - [\,e'\,] + 2\,[\,O_i''\,] \tag{5}$$

Mere acceptor doping as well as mere donor doping was well investigated for ceria in the past. Donor dopants such as Ta^{5+} lead to a predominating n-type conduction in the lattice mainly compensated by the positive donor charges and suppressing the ionic defects, i.e. leading to low concentrations of vacancies and interstitials [17]. Acceptor dopants such as Sr^{2+} primarily cause compensation by high vacancy concentrations; on the other hand they suppress n-type electronic defects. Consequently, donor doped ceria shows good electronic conductivity of the order of 10-3 S/cm at 600 ℃ [17]. On the other hand, high concentrations of acceptor doped ceria show very good oxygen ion conductivities up the order of 10^{-2} S/cm at 600 ℃ and higher.

In this work, we aim at an analysis of the intrinsic point of nominally pure ceria which usually contains a certain impurity level at or below about 0.1 to 0.01 mole %. However, it is not clear whether nominally pure ceria is net acceptor or donor doped. It should be possible to answer this question by a sort of dopant titration, i.e. analyzing the total conductivity starting from a certain level of donor concentration and increasing the

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[1] All represented symbols are in form of Kröger Vink notation.

concentration of an acceptor dopant in small steps (or vice versa). One expects a minimum of the total ionic and electronic defect concentrations at the intrinsic point due to the compensation of donor and acceptor doping as the latter is theoretically defined by the condition

$$[Ta_{Ce}^{\bullet}] - 2[Sr_{Ce}''] = 0 \qquad (6)$$

The conductivity minimum should appear very near to this point, although it will not exactly coincide with this as the mobilities of the electronic and ionic charge carriers are different. As the mobility of electrons, in general, is larger than that of the oxygen ions (vacancies or interstitials) the minimum of the total conductivity should occur for a slight excess of the acceptor dopant.

3. Experimental Procedure

Samples with the corresponding oxides of Ce, Sr and Ta were prepared using solid state mixing route. CeO_2 (Sigma Aldrich, 99.9%), SrO (Sigma Aldrich, 99.99%) and Ta_2O_5 (ABCR GmbH, 99.98%) were taken and ball milled using zirconia balls for 4 h in the presence of acetone as medium. Prepared mixtures were dried in an oven at 70 ℃ for 24 h and then kept at 150 ℃ for 2 h. Dried powder was pressed in pellets form with the help of uni-axial press and pellets were sintered at 1500 ℃ for 6 h. During sintering schedule the temperature was also kept constant for 2 h at 1000 ℃ in both of the directions of sintering program keeping the heating and cooling rate 150 ℃ throughout. Sintered pellets had the diameter of around 0.7 cm and thickness of around 0.15 cm. Sintered pellets were polished for a small time just to remove the oxide layers from the surfaces of pellets. Density of the samples were measured with the help of Archimedes principle and then compared with the theoretical values (shown in table.1). X-ray powder diffraction has been carried out with Cu K_{α} radiation.

Impedance analysis was applied to determine the total conductivity. The contributions of grain boundaries and the bulk phase were carefully separated by analysis of the frequency dependence as visualized with the help of complex plane plots (cole-cole plots). The resulting bulk conductivities were plotted logarithmically versus the inverse temperature. The resulting Arrhenius plots were used as usual to derive the activation energies Impedance measurements to determine the total conductivity and activation energy were carried out for all the samples with the help of an integrated NOVOCONTROL high frequency analyzer impedance set-up.

Table.1. Calculation for % densities for the samples $Ce_{0.97-x}Sr_xTa_{0.03}O_{2-\delta}$ with different values of 'x':

x	Lattice parameter (A)	Molecular weight, M (gm/mole)	Theoretical density ρ_{th} (gm/cm^3)	Experimental density ρ_{ex} (gm/cm^3)	% Density
0.00	5.366	173.572	7.461	6.957	93.24
0.01	5.354	175.017	7.574	6.987	92.24
0.02	5.351	172.211	7.463	6.998	93.77
0.03	5.345	171.526	7.457	6.874	92.18
0.04	5.331	170.841	7.487	6.834	91.28
0.05	5.333	170.156	7.449	6.976	93.65

4. Results and Discussion

4.1. X-ray diffraction analysis

X-ray diffraction patterns for all the prepared samples are shown in Fig. 1 which shows that only single phase was present in all the samples. This means that all the dopants are soluble in ceria lattice but for the sample with 5% Sr it can be seen that some very small features around 30-33 degree started to appear[2]. It could mean that this much amount might be the limit of solubility of these dopants in ceria and a further increase in amount of dopants may cause a multiphase material. Therefore, the present investigation is limited to the maximum amount of Sr and Ta in ceria as 5% and 3% respectively. XRD also shows that the

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[2] The detection limit of XRD is around 3% of a phase.

peaks shifted towards the higher theta values with increase in doping concentration of Sr^{2+} which decreases the lattice parameter as shown in table.1.
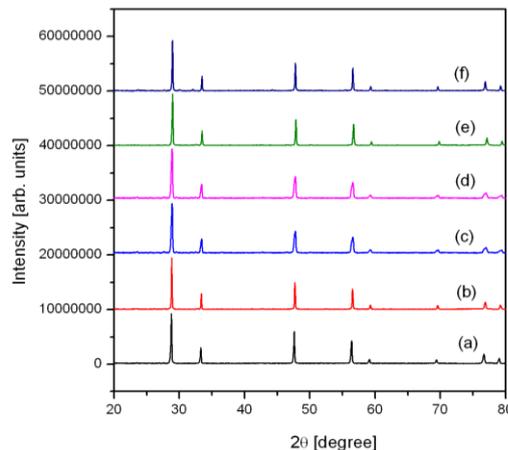

Fig. 2. X-ray powder diffraction patterns for $Ce_{0.97-x}Sr_xTa_{0.03}O_{2-\delta}$ with x = (a) 0.00, (b) 0.01, (c) 0.02, (d) 0.03, (e) 0.04 and (f) 0.05

4.2. Impedance analysis

In present work, the compositions are prepared within the limits of solubility of these dopants in ceria. A direct comparison of the total conductivities for Sr (1-5%) + Ta (3%) doped ceria is shown in fig.2. This would be the combined effect of acceptor and donor dopants in ceria lattice. It may be seen that the total conductivity for 3% Ta doped ceria is the maximum and as the amount of Sr is doped in it, conductivity starts getting lower down till 4% amount of Sr. Further increase of Sr causes an increase in total conductivity. It seems that the dopants are cancelling the effect of each other because of having opposite defect contribution. Ta and Sr doped ceria are reported as good electronic [18] and good ionic [19] conductors respectively. A small doping of Sr would cause a small number of oxygen ion vacancies which might cancel out the effect of Ta doping till a little extant. This results in decrease of total conductivity. As the amount of Sr increases, total conductivity decreases accordingly and attains a minimum value for $Ce_{0.93}Sr_{0.04}Ta_{0.03}O_{2-\delta}$ composition but again increases with further increase in Sr^{2+}. The reason may be, as soon as Sr^{2+} neutralizes the effect of Ta^{5+} completely, further increase in its amount introduces its own effect which increases the oxygen ion vacancies and in turn oxygen ion conductivity. This increase in ionic conductivity causes an increase in total conductivity.
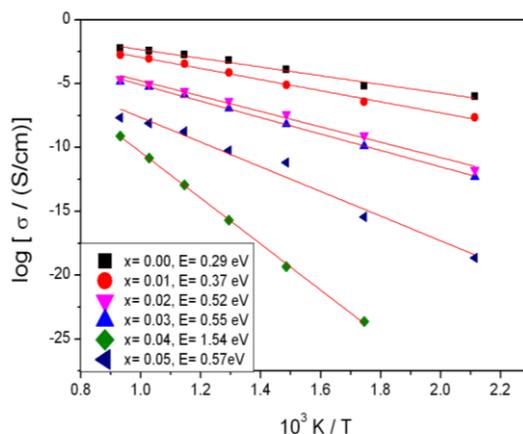

Fig. 2. Conductivity variation of $Ce_{0.97-x}Sr_xTa_{0.03}O_{2-\delta}$ with temperature and calculated activation energies 'E'

According to the mentioned theoretical approach, approximately 1.5% Sr^{2+} should cancel the effect of 3% Ta^{5+} and further doping of Sr^{2+} should cause an increase in ionic conductivity and therefore in total conductivity. But experiment shows that 1.5% Sr^{2+} is not enough to cancel the effect of 3% Ta^{5+} but this limit is somewhere near 4% Sr^{2+} because more than this amount of Sr^{2+} causes an increase in total conductivity. This investigation suggests that even pure ceria contains a small amount of donor dopant. This amount might not enough to introduce electronic conductivity in ceria in intrinsic form but it has a noticeable effect in present work. This may also be the reason that ceria has a small ionic conductivity in intrinsic form. Activation energy also changes in accordance with the amount of Sr dopant, it is the minimum for 3% Ta doped ceria (0.29 eV) and increases with the doping of Sr. Activation energy reaches at its maximum for $Ce_{0.93}Sr_{0.04}Ta_{0.03}O_{2-\delta}$ (1.54 eV). Further increase in the amount of Sr causes again a decrease in activation energy for $Ce_{0.92}Sr_{0.05}Ta_{0.03}O_{2-\delta}$ (0.57 eV).

5. Conclusion

The complementary effects of acceptor dopant on donor doped ceria were clearly identified and proven by the minimum of the total conductivity. Adding an acceptor dopant, Sr^{2+}, to a donor doped sample opposes the effect of the donor and therefore, decreases the total conductivity. It was theoretically suggested that we should have got the minimum total conductivity i.e. maximum neutralization of the effect of Ta^{5+} by Sr^{2+} at around 1.5% of Sr doping but experimental results have shown a shift of the observed total conductivity to a higher concentration of 4 mole % Sr^{2+} , i.e. the composition $Ce_{0.93}Sr_{0.04}Ta_{0.03}O_{2-\delta}$. Although part of this observation is due to the higher mobility of electrons in a donor doped situation, the effect is still too large to be explained by the mobility difference only. It is assumed that the nominally pure ceria in fact exhibits a non-negligible amount of donor dopant. As the amount of Sr^{2+} is further increased, presence of Sr^{2+} starts dominating over the Ta^{5+} donor which results in an increase of the total conductivity.

6. Acknowledgement

7. References

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