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Electrical Conductivity and Thermal Expansion of Ceria Doped with Pr, Nb and Sn

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Abstract

The effect of Pr, Nb and Sn substitution on the electrical conductivity, thermal expansion and the structure of the phases formed was investigated in a series of samples based on ceria solid solutions. X-Ray diffraction (XRD) analysis was performed in order to study the phase content and to measure the cell lattice parameters. Electrical conductivity was measured in air by means of the four-point DC technique, within the temperature range 400–1000°C. Also, thermal expansion coefficient measurements were carried out using the dilatometer technique. The results show that doping of ceria with 8–10 mol% praseodimia increases the electrical conductivity, while the addition of Nb_2O_5 leads to the formation of a second, monoclinic, phase which decreases the conductivity. The thermal expansion coefficient in Pr-doped ceria is $8 \times 10^{-6}/K$ at temperatures lower than 500°C, then it increases to $10–11 \times 10^{-6}/K$ at 900°C. Doping with Nb_2O_5 eliminates the increase of thermal expansion at high temperatures. Sn was found to be a possible substitute for Ce in ceria solid solutions.

Der Effekt von Pr-, Nb- und Sn-Substitution auf die elektrische Leitfähigkeit, die thermische Ausdehnung und die Struktur der sich bildenden Phasen wurde an einer Serie von Proben untersucht, die auf Zeriumoxid-Mischkristallen basieren. Mit Hilfe der Röntgenbeugung (XRD) wurden der Phasenanteil und die Gitterparameter untersucht. Die elektrische Leitfähigkeit wurde in einem Temperaturbereich zwischen 400 und 1000°C an Luft mit Hilfe der Vierpunkt DC-Technik gemessen. Die Bestimmung des thermischen Ausdehnungskoeffizienten erfolgte dilatometrisch. Die Ergebnisse zeigen, daß Zeriumoxid, dotiert mit 8–10 Mol% Praseodimia, eine höhere elektrische Leitfähigkeit besitzt, während die Zugabe von Nb_2O_5 zur Bildung einer zweiten monoklinen Phase führt, die die Leitfähigkeit vermindert. Der thermische Ausdehnungskoeffizient von Zeriumoxid dotiert mit Pr beträgt $8 \times 10^{-6}/K$ bei Temperaturen unterhalb von 500°C und steigt auf $10–11 \times 10^{6}/K$ bei 900°C an. Dotieren mit Nb_2O_5 eliminiert die Zunahme der thermischen Ausdehnung bei hohen Temperaturen. Sn ist ein möglicher Substituent für Ce in Zeriumoxid-Mischkristallen.

L'effet du dopage avec Pr, Nb, et Sn sur la conductivité électrique, la dilatation thermique et la structure des phases crystallines formées a été étudié dans une série d'échantillons de solutions solides à base de cérie. L'analyse par diffraction de rayons-X a été utilisée pour étudier le contenu en phases cristallines et mesurer leur paramètres de maille. La conductivité électrique a été mesurée dans l'air entre 400 et 1000°C avec la technique des quatre points en courant continu. Enfin, la dilatation thermique a été mesurée à l'aide d'un dilatomètre. Les résultats montrent que le dopage de la cérie avec 8 à 10 mol% d'oxide de praseodimium augmente la conductivité électrique tandis que l'ajout de Nb_2O_5 conduit à la formation d'une deuxième phase, monoclinique, qui décroît la conductivité. Le coéfficient de dilatation thermique dans la cérie dopée au Pr est $8 \times 10^{-6}/K$ pour des températures inférieures à 500°C et il augmente jusqu'à $10–11 \times 10^{-6}/K$ à 900°C. Le dopage avec Nb_2O_5 élimine l'augmentation de la dilatation thermique à hautes températures. Sn a montré d'être un possible élément de substitution pour Ce dans des solutions solides de cérie.

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1 Introduction

Oxygen ion conductors have been demonstrated as prominent ceramic oxides incorporated in many technological devices operating at elevated temperatures that require to be sustained by high oxygen transport. Examples include mixed conductors for ceramic membranes designed to separate oxygen from air[1-5] and oxide electrodes for solid oxide fuel cells (SOFC), electrolysers, oxygen pumps and amperometric oxygen monitors.[6-12]

So far, oxygen ion conductivity has been reported for many oxide systems.[13-19] Most of them crystallise either in the perovskite structure or in the fluorite structure. The latter includes oxides like ZrO_2, ThO_2, CeO_2 and Bi_2O_3. Among these pure compounds, only in ceria and thoria is the fluorite structure stable from room temperature up to their melting points. Zirconia and bismuth oxide undergo a number of polymorph transformations in different temperature ranges.

The well-known ionic conductivity of the stated oxides, particularly of ZrO_2, ThO_2 and CeO_2 is greatly enhanced when doped with lower valent metal oxides, due to the creation of excess oxygen vacancies.[20-29] The solid solutions of CeO_2 and ThO_2 have also provided a fertile subject for the development of theoretical models.[30,31]

Though many aliovalent cations have been extensively examined in respect of their doping effect on the electrical conductivity of ceria, there are very few data concerned with the role of praseodymia, niobia and tin oxides. The present work is intended to investigate the effect of Pr, Nb and Sn substitution for Ce in the ceria solid solution on the electrical conductivity, thermal expansion and the structure formed.

2 Experimental

Four solid oxide solutions based on CeO_2 were synthesised (A, B, C, D) by partial substitution of Ce with Pr, Nb and Sn, as shown in Table 1. The starting materials used were CeO_2, Pr_6O_{11}, Nb_2O_5 and SnO_2, all of a purity higher than 99·9%. The samples were prepared by the solid oxide route. The required proportions of the raw oxides were dispersed in acetone, milled for 10 h and evaporated under stirring until dryness. Calcination was performed at 1100°C for 12 h. After grinding, the calcined powders were pressed into bars under a uniaxial stress of 300 MPa and sintered in air for 30 h. The sintering temperature was 1450°C for sample C, containing Nb_2O_5, and 1550°C for samples A, B and D. The heating and cooling rate was 5°C/min. The bulk density of all the sintered samples was more than 90% of the theoretical density.

XRD analysis was performed with a Philips PW 1710 diffractometer and Cu-K_α radiation. The diffractometer was operated at 40 kV and 40 mA. XRD spectra were obtained by scanning continuously at a rate of 1°2θ/min and using Ag as internal standard. The cell parameters were calculated using a least squares refinement program.

The electrical conductivity was monitored in the temperature range of 400 to 1000°C by using the four-point probe DC technique. Also, thermal expansion measurements were carried out by means of the dilatometer technique up to 1000°C.

3 Results and Discussion

The XRD study showed that the samples $Ce_{0.90}Pr_{0.10}O_{1.95}$ (A) and $Ce_{0.92}Pr_{0.08}O_{1.96}$ (B) contain a single phase consisting of the cubic fluorite structure (MO_2). The sample $Ce_{0.87}Pr_{0.08}Nb_{0.05}O_{1.96}$ (C) consists mainly of the same fluoride structure but a minor phase with monoclinic structure attributed to the fergusonite phase ($CeNbO_4$) is also present.

In composition C, the authors attempted to substitute 50 mol.% of Sn for Ce, presented as sample D, $(Ce_{0.50}Sn_{0.50})_{0.87}Pr_{0.08}Nb_{0.05}O_{1.96}$. By

Table 1. Composition, lattice parameters and crystal structure of the oxides prepared

Code	*Composition*	*Lattice parameters (Å)*	*Crustal structure*
A	$Ce_{0.90}Pr_{0.10}O_{1.95}$	$a = 5.411\,5$ (6)	Cubic
B	$Ce_{0.92}Pr_{0.08}O_{1.96}$	$a = 5.412\,0$ (3)	Cubic
C	$Ce_{0.87}Pr_{0.08}Nb_{0.05}O_{1.96}$	$a = 5.413\,0$ (6)	Cubic
		$a = 5.553\,1$ (6)	Monoclinic
		$b = 11.360\,2$ (5)	
		$c = 5.148\,2$ (5)	
		$\beta = 94.48$ (1)°	
D	$(Ce_{0.50}Sn_{0.50})_{0.87}Pr_{0.08}Nb_{0.05}O_{1.96}$	$a = 5.408$ (1)	Cubic (fluorite)
		$a = 10.545$ (2)	Cubic (pyrochlore)
		$a = 5.605$ (2)	Monoclinic
		$b = 11.348$ (1)	
		$c = 5.141$ (1)	
		$\beta = 93.28$ (1)°	

firing the sample D at 1450°C for 30 h in air, the main phases formed had the fluorite and the pyrochlore structure ($A_2B_2O_7$). Also, as a minor constituent, the phase with the monoclinic structure was present. After raising the temperature to 1550°C and sintering for 10 h, the pyrochlore phase content could be reduced to lower levels in favour of a higher content of the fluorite phase. This suggests that Sn could replace Ce in the fluorite structure for lower substitutions than 50 mol.%, which will be the subject of future investigation. The crystal structure and the cell parameters calculated for the phases formed in the specimens A, B, C, D are referred to in Table 1. In all the cases, no significant differences in the lattice parameters of the fluorine structure are observed.

In a mixed conductor, when electronic and ionic conductivity magnitudes are comparable, the electrical conductivity (σ) measured by the four-point DC technique is referred to the sum of ionic and electronic conductivity. The results obtained are shown in Fig. 1. The samples A and B, having the single phase with the fluorite structure, present higher conductivity than pure ceria,[27] promising well for the higher ranges of substitution. Three temperature regions are observed, a low temperature region with an apparent activation energy, E_a of 89 and 101 kJ/mol, an intermediate region where small or no increase in the conductivity is observed and a high region with E_a 77 and 86 kJ/mol for the specimens A and B respectively. The variation of Pr content from 8 to 10 mol.% does not have an appreciable influence on the conductivity. These results are in good agreement with conductivity measurements reported by Takasu *et al.*[27] with an AC technique. The activation energy observed for Pr-doped ceria is about double that observed in pure ceria for small polarons conduction (electronic

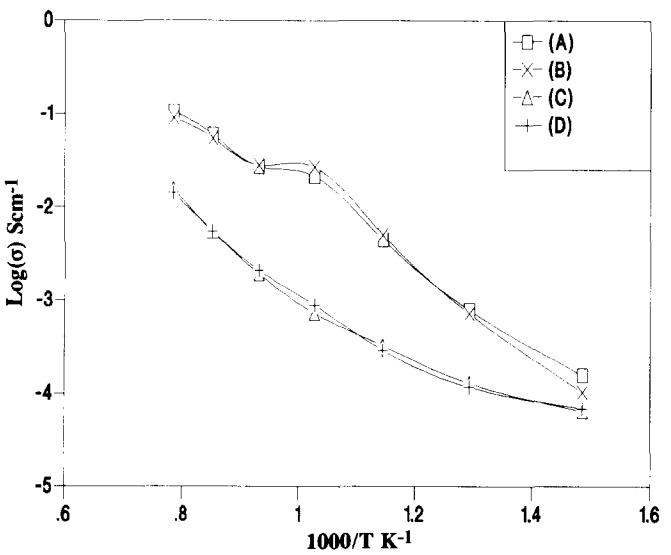

Fig. 1. Electrical conductivity (σ) of the compositions prepared versus reciprocal temperature.

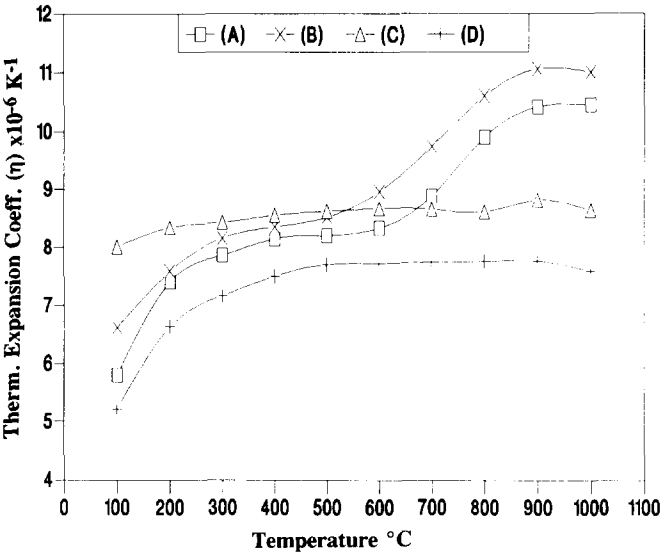

Fig. 2. Thermal expansion coefficient (η) of the oxides prepared versus temperature.

conduction),[22-24] suggesting that different mechanisms contribute to the total conductivity.

As far as the compositions containing Nb and Sn are concerned, samples C and D show almost similar conductivities, and are one order of magnitude lower than those of A and B. This decrease can be mainly attributed to the presence of the monoclinic phase.[24]

Results of thermal expansion coefficient (η) are shown in Fig. 2 as a function of temperature. These results indicate that thermal expansion of ceria doped with 10 and 8 mol.% Pr (samples A and B respectively) is about 20% lower than for pure ceria ($\eta = 9{\cdot}7 \times 10^{-6}/K$[32]) in the low temperature region (< 500°C). Starting from 500°C the thermal expansion of these two compositions increases from $8 \times 10^{-6}/K$ to $10{\cdot}5 \times 10^{-6}/K$ (A) and $11 \times 10^{-6}/K$ (B) at 900°C. The thermal expansion appears to be constant again from 900 to 1000°C. The thermal expansion is likely to be due to the loss of oxygen and the increased concentration of Pr^{3+} which has a sensibly higher cation radius than Pr^{4+} (1·28 Å for Pr^{3+} and 1·10 Å for Pr^{4+} for coordination number VIII.[33] The thermal expansion of C and D compositions are given by the contribution of three different phases (fluorite as a main phase, pyrochlore and monoclinic as minor phases). The addition of Nb in these samples seems to be responsible for the absence of an increase of thermal expansion between 500 and 900°C. While material C shows a comparable thermal expansion to materials A and B for temperatures lower than 600°C, the addition of Sn, sample D, reduces the thermal expansion coefficient to $7 \times 10^{-6}/K$. The observed thermal expansion coefficients suggest that Pr-doped ceria solid solutions might be used as electrode materials for solid oxide fuel cells with zirconia electrolyte ($\eta = 10 \times 10^{-6}/K$).

4 Conclusions

Doping of CeO_2 with Pr remarkably enhances the electrical conductivity and reduces thermal expansion. The addition of Nb_2O_5 improves the sintering of the present ceramics. However, the content used (5 mol%) was too high, resulting in the formation of the monoclinic phase with the fergusonite structure, which reduces the conductivity. SnO_2 was found to be a promising candidate for ceria substitution.

Thus, both the low thermal expansion coefficient and the good electrical conductivity found, classify the present doped ceria ceramics as good candidates for further investigations with respect to their technological applications as oxide electrodes.

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