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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 4283–4286
www.elsevier.com/locate/jeurceramsoc

Effects of Fe-additions on sintering and transport properties of $Yb_2Ti_{2-y}Fe_yO_{7-\delta}$

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Abstract

Partial substitution of Fe for Ti in $Yb_2Ti_{2-y}Fe_yO_{7-\delta}$ has been used to improve the sinterability of these ion conducting pyrochlore-type materials, and to adjust their transport properties. Fe additions displace the maximum shrinkage rate to lower temperatures and allow the preparation of dense materials at lower firing temperatures. Impedance spectroscopy was used to de-convolute the effects of Fe additions on the bulk and grain boundary conductivities. The bulk conductivity was enhanced for relatively low Fe additions (<5%) and its activation energy was lowered. The grain boundary conductivity was also enhanced. The dependence of total conductivity on oxygen partial pressure shows that this enhancement corresponds to ionic conductivity. The onset of n-type conductivity is displaced to more reducing conditions with Fe addition.

Keywords: Grain boundaries; Electrical conductivity; Impedance; Ionic conductivity; Pyrochlore

1. Introduction

$Yb_2Ti_2O_7$ is an interesting model for materials with the pyrochlore structure. These materials are potential solid electrolytes for high temperature electrochemical applications.[1] However, their transport properties are often far from optimized, thus requiring composition changes to adjust the transport properties. For example, prospective applications of $Yb_2Ti_2O_7$-based materials require an increase of ionic conductivity and suppression of n-type conductivity under reducing conditions. This residual n-type contribution may be partially lowered in Yb-rich compositions.[2] However, this type of composition change also causes a decrease in ionic conductivity. Other ways to modify pyrochlore-type materials and their properties is by partial substitution in the A- and B-site positions with aliovalent additives. The wide ranges of valence accommodated in A-site and B-site positions is revealed by the original pyrochlore $NaCaNbTaO_6(O, OH, F)$ and suggests possibilities of partial substitution of trivalent Yb^{3+} by acceptor-type dopants such as A^{2+} and possibly even A^{+} species. Similarly, the tetravalent Ti^{4+} may be replaced by trivalent acceptors. Partial substitution with a pentavalent species is likely to play the opposite effect, i.e. to enhance the electronic (n-type) conductivity. Note that the main requirement for partial substitution is often related to the cationic radii of prospective A- and B-site species. For example, the combination of a large A-site acceptor species with a relatively small B-site cation is unlikely to fit the pyrochlore structure and often instead favors the formation of the perovskite phase.

Anti-site occupancy can also introduce charged point defects, as found for off-stoichiometric compositions $Yb_2(Ti_{2-x}Yb_x)O_{7-\delta}$[2]; this possibility is probably restricted to cations with intermediate ionic radii, to allow its insertion in BO_6 octahedra. The Yb excess is thus expected to act as acceptor species as described by:

$$\begin{aligned}&(2-x)TiO_2 + (1+0.5x)Yb_2O_3\\ &\quad \rightarrow (2-x)Ti_{Ti}^{x} + xYb_{Ti}' + 2Yb_{Yb}^{x}\\ &\qquad + (7-0.5x)O_O^{x} + 0.5xV_O^{\bullet\bullet} \end{aligned} \tag{1}$$

Somewhat surprisingly, these materials with Yb excess show poorer ionic conductivity when compared to the stoichiometric composition,[2] probably due to a decrease in mobility, caused by relatively large YbO_6 octahedra. The ionic conductivity of this type of materials can also be affected by order–disorder transformations.[3,4] Phase transformation of pyrochlore-type materials tends to be induced by lowering the difference between the average cationic sizes of A and B site species, which favours

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0955-2219/$ – see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2007.02.133

formation of disordered fluorite type-materials, as observed for $Y_2(Ti, Zr)_2O_7$ with similar fractions of Zr and Ti.[4,5] In this case, the average radii of B-site species approaches that of A-site Y^{3+}. A similar finding was found by partial substitution on the A-site with smaller cations, as for $(ScYb)_2Ti_2O_7$.[6] It is also believed that order–disorder transformations in pyrochlore-type materials may be promoted independently in the anionic and cationic sub-lattices.[4,7] By analogy with defect interactions in fluorite structures one may thus assume that negatively charged Yb'_{Ti} may interact with positive charge carriers (oxygen vacancies), affecting the ionic conductivity due to defect clustering:

$$Yb'_{Ti} + V_O^{\bullet\bullet} \leftrightarrow (Yb_{Ti}V_O)^{\bullet} \quad (2)$$

The purpose of the present work is to study alternative composition changes based on additions of an acceptor species. One expects significant partial substitution of Ti by Fe, based on the similarity between the ionic radius of Ti^{4+} and Fe^{3+} with coordination 6. One can assume that trivalent Fe^{3+} predominates as for other ferrite-based materials with typical six-fold coordination (e.g. perovskites). The effects on the defect chemistry can thus be described by:

$$\begin{aligned}&(2-y)TiO_2 + (y/2)Fe_2O_3 + Yb_2O_3\\ &\quad \rightarrow (2-y)Ti_{Ti}^x + yFe'_{Ti} + 2Yb_{Yb}^x\\ &\qquad + (7-y/2)O_O^x + (y/2)V_O^{\bullet\bullet}\end{aligned} \quad (3)$$

Simultaneously, this acceptor-type additive may affect the reducibility thus reverting the reaction of formation of electronic species:

$$O_O^x \xleftrightarrow{k_{red}} \tfrac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e' \quad (4)$$

2. Experimental

$Yb_2Ti_{2-y}Fe_yO_{7-y/2}$ materials, with $y=0$, 0.05, 0.1 and 0.2 were prepared by solid state reaction of powder mixtures (Yb_2O_3, TiO_2 and Fe_2O_3). These were calcined at 1000 °C for 5 h with repeated intermediate regrinding and calcinations steps. The resulting powders were then uniaxially pressed at 10 MPa, sintered at 1600 °C for 5 h, and then cooled at 1 °C/min. This minimizes the risk of uncontrolled effects related to differences in thermal history. Calcined powders and crushed samples were characterized by X-ray diffraction, while scanning electron microscopy was used for microstructural characterisation, including evaluation of grain size distribution and average grain sizes, estimated by the image processing technique ASTM E1382-97.[8]

Impedance spectroscopy at temperatures in the range of 300–900 °C was used to de-convolute the bulk and grain boundary contributions of the overall electrical behaviour, using a Hewlett Packard 4284A bridge, in the frequency range of 20–10^6 Hz using Pt electrodes. The dependence of total conductivity as a function of oxygen partial pressure was used to estimate the ionic conductivity and the onset of the n-type electronic contribution in reducing conditions.

Table 1
Lattice parameter, average grain size and activation energy values for the bulk (B) and grain boundary (gb) conductivities of $Yb_{2+y}Ti_{2-y}O_{7-y/2}$ sintered at 1600 °C

y	a_0 (nm)	Grain size (μm)	$E_{\sigma,B}$ (kJ/mol)	$E_{\sigma,gb}$ (kJ/mol)
0	10.025	5.4	85	130
0.05	10.032	5.6	64	108
0.1	10.028	8.9	65	98
0.2	10.033	10.3	91	–

3. Results and discussion

XRD results showed that $Yb_2Ti_{2-y}Fe_yO_{7-y/2}$ samples with partial substitution of Ti by Fe are single phase, without evidence of secondary phases. Partial substitution of Ti by Fe facilitates sintering at lower temperatures. SEM micrographs show no evidence of secondary phases and a gradual increase in average grain size with increasing content of Fe (Table 1). Furthermore, the materials remained stable after exposition to typical fuel conditions, showing that reducibility does not affect the stability of the actual materials, for both the stoichiometric composition and after partial substitution of Ti by Fe.

Although, Eqs. (1) and (3) predict that excess of Yb and additions of Fe exert similar effects on the defect chemistry, the corresponding structural and microstructural changes may differ significantly. For example, non-stoichiometric samples $Yb_{2+x}Ti_{2-x}O_{7-x/2}$, fired in identical conditions to the stoichiometric composition, showed decreasing grain size and extensive lattice expansion with increasing excess of Yb,[2] probably because anti-site occupancy yields large YbO_6 octahedra, increasing lattice parameter.

At intermediate temperatures (Fig. 1) the impedance spectra show separate contributions for bulk and grain boundary behaviour. These contributions are distinguished due to major differences in capacitance and relaxation frequencies. At higher temperatures, the increase in conductivity displaces the relaxation frequency of the bulk behaviour to values above 1 MHz. In these cases, spectra only reveal the transition from the bulk to grain boundary contributions due to experimental limitations.

By fitting the impedance spectra one obtained the bulk and grain boundary conductivities (Fig. 2a and b). These results show that the bulk conductivity only increases for small additions of Fe, while the trend is reverted for higher contents. A similar

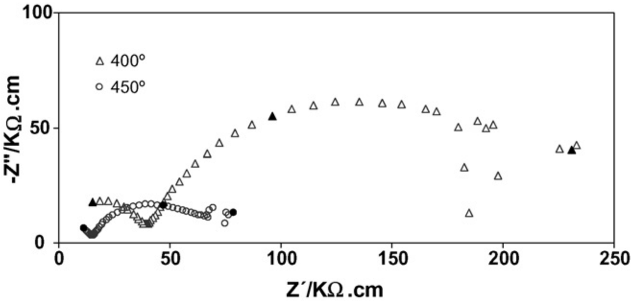

Fig. 1. Impedance spectra of $Yb_2Ti_{1.9}Fe_{0.1}O_{6.95}$ sintered at 1600 °C and measured at 400 and 450 °C, in air. Solid points indicate data at 20 Hz, 1000 Hz, and 10 MHz.

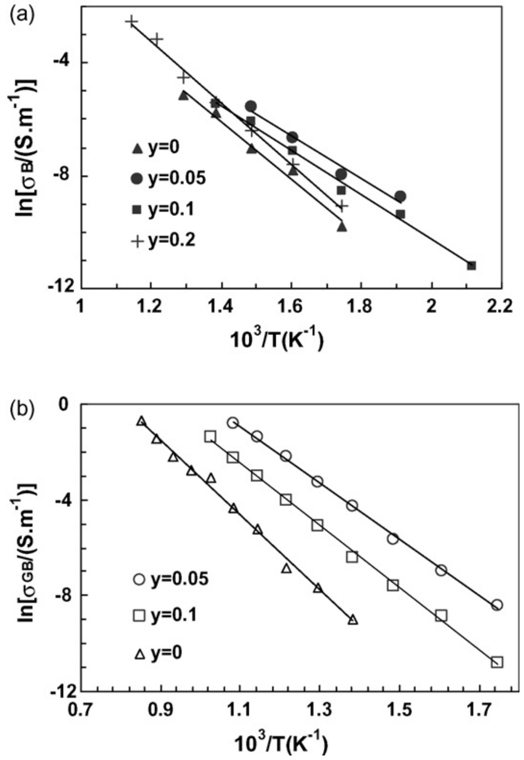

Fig. 2. (a) Bulk and (b) grain boundary conductivities corrected for the area thickness ratio of $Yb_2Ti_{2-y}Fe_yO_{7-y/2}$.

conductivity trend is observed for the grain boundary, (Fig. 2b). Although increasing Fe contents yield improvements in grain boundary conductivity, this effect is irrelevant at high operation temperatures, due to differences in the temperature dependence. This is emphasized by differences in activation energy (Table 1).

Changes in ionic conductivity can be related to differences in charge carrier concentration $[V_O^{\bullet\bullet}]$ and/or differences in mobility μ_V, as described by:

$$\sigma_I = 2e[V_O^{\bullet\bullet}]\mu_V \tag{5}$$

The increase in concentration can explain the increase in bulk conductivity for relatively small fractions of Fe. However, this is not followed for higher Fe contents (Fig. 2a), thus indicating a decrease in mobility or trapping of charge carriers. One can account for the increase in activation energy of bulk conductivity (Table 1) by estimating the nominal mobility $\mu_{V,nom} = \sigma_I/(2e[V_O^{\bullet\bullet}]_{nom})$, where the nominal charge carrier concentration was estimated on assuming that Fe is mainly trivalent, with predominant ionic defects (Fig. 3). Note that other titanates with the perovskite structure also show strong nonlinearity of ionic conductivity on adding Fe. The coordination of B-site (6) species is identical in both cases. For example, oxygen vacancies can be trapped by aliovalent Fe^{3+} or Fe^{2+} cations in $CaTi_{1-y}Fe_yO_{3-\delta}$, as revealed by changes in coordination[9]; this corresponds to a major decrease in the effective concentration of charge carriers on exceeding an optimum fraction of Fe. Excess of Yb also leads to a decrease in bulk conductivity,[2] possibly because the structural changes caused by large YbO_6 octahedra lower the mobility of oxygen vacancies, or promote strong interactions between the trivalent B-site species and oxygen vacancies, as found for fluorite materials with high contents of trivalent additives.[10]

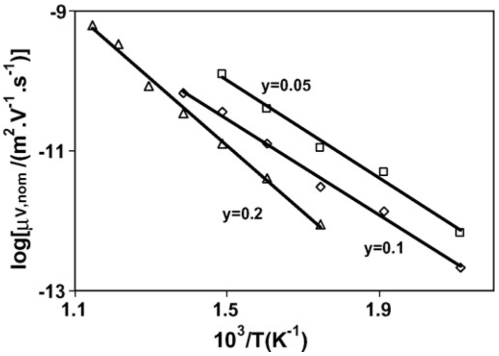

Fig. 3. Estimated values of mobility based on the bulk conductivity in air and nominal concentration of oxygen vacancies for $Yb_2Ti_{2-y}Fe_yO_{7-y/2}$ materials with $y = 0.05$, 0.1, and 0.2.

Fig. 4 compares the oxygen partial pressure dependence of total conductivity for Fe-containing compositions to the Fe-free composition. The plateau in Fig. 4 suggests that ionic transport predominates in oxidizing and intermediate conditions of oxygen partial pressure. In fact, one does not expect a significant dependence of ionic conductivity on the oxygen partial pres-

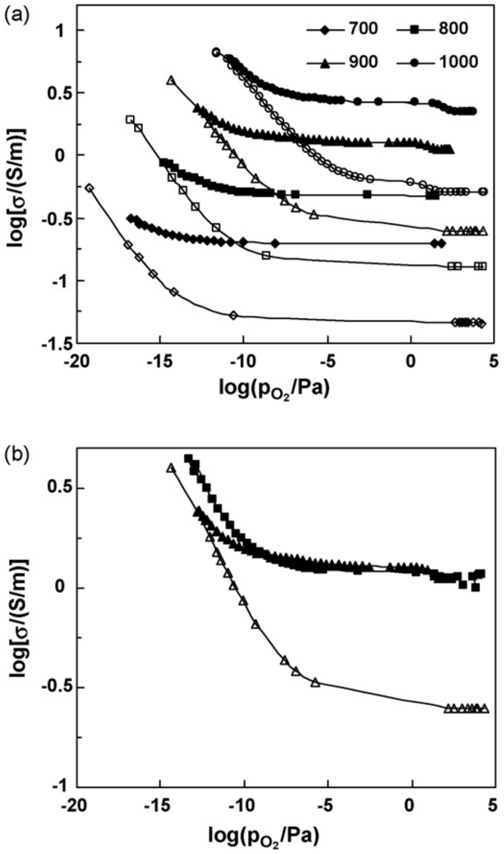

Fig. 4. (a) Total conductivity of $Yb_2Ti_2O_7$ (open symbols) and $Yb_2Ti_{1.9}Fe_{0.1}O_{6.95}$ (closed symbols) at 700, 800, 900 and 1000 °C. (b) Total conductivity of $Yb_2Ti_{2-y}Fe_yO_{7-y/2}$ at 900 °C, with $y = 0$ (triangles), $y = 0.05$ (filled triangles) and $y = 0.1$ (squares).

sure and Eq. (4) suggests a −1/4 power law for the electronic conductivity if one assumes nearly constant concentration of oxygen vacancies; this yields the following dependence of total conductivity:

$$\sigma = \sigma_{\mathrm{I}} + \sigma_{n,1} p_{\mathrm{O}_2}^{-1/4} \tag{6}$$

The dependence is nearly true for the Fe-free composition.

Fig. 4a thus shows that partial substitution of Ti by Fe raises the ionic plateau and displaces the onset of electronic conductivity to more reducing conditions, as expected on combining Eqs. (3) and (4). Although the ionic plateau of the stoichiometric composition $Yb_2Ti_2O_7$ is about one order of magnitude lower than the conductivity of a standard YSZ electrolyte, this difference decreases with additions of Fe. In addition, the activation energy is significantly lower for $Yb_2Ti_{2-y}Fe_yO_{7-y/2}$ with $y = 0.05$–0.1 (Table 1), showing that the actual materials can compete with YSZ at intermediate temperatures. Further progress is expected by optimizing the Fe content.

Fig. 4b also shows that Fe-containing compositions suppress the onset of n-type conductivity in typical fuel conditions, thus confirming the acceptor-type behaviour of additions of Fe. Very reducing conditions are likely to cause at least partial reduction of Fe^{3+} to Fe^{2+} and thus coexistence of both valence states. In fact, the pyrochlore structure easily accommodates significant fractions of larger B-site cations without collapsing, except possibly for partial order–disorder transformation. This may explain the good stability of these materials even when the transport properties reveal significant reducibility. Since the actual fractions of Fe are relatively small, co-existence of Fe^{3+} and Fe^{2+} is probably insufficient to allow significant hopping between these species in $Yb_2Ti_{2-y}Fe_yO_{7-y/2}$.

4. Conclusions

Partial substitution of Ti by Fe has advantages in terms of enhanced sinterability and improvement of transport properties of potential electrolyte materials based on $Yb_2Ti_2O_7$. Small additions of Fe enhance the bulk conductivity of pyrochlore-type $Yb_2Ti_{2-y}Fe_yO_{7-\delta}$, and contribute to lower the grain boundary resistance. Reducibility is also hindered by displacing the onset of the n-type contribution to very reducing conditions. The dependence of total conductivity on oxygen partial pressure suggests that these materials are nearly pure ionic conductors in air. The beneficial effects on ionic conductivity by Fe additions are spoiled for excessive contents of Fe, possibly due to electrostatic interactions between the additive and oxygen vacancies. The dependence of total conductivity on oxygen partial pressure shows that these materials are nearly pure ionic conductors in air. Differences in activation energy of bulk conductivity in air indicate that Fe causes an increase in the concentration of oxygen vacancies.

Acknowledgements

This work was supported by FCT, Portugal, in the form of grants SFRH/BD/10958/2002 and SFRH/BPD/3529/2000.

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