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Acceptor doping of $Ln_2Ti_2O_7$ (Ln = Dy, Ho, Yb) pyrochlores with divalent cations (Mg, Ca, Sr, Zn)

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ABSTRACT

New LANTIOX high-temperature conductors with the pyrochlore structure, $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn; x = 0, 0.01, 0.02, 0.04, 0.07, 0.1), have been prepared at 1400–1600 °C using mechanical activation, co-precipitation and solid-state reactions. Acceptor doping in the lanthanide sublattice of $Ln_2Ti_2O_7$ (Ln = Dy, Ho, Yb) with Ca^{2+} , Mg^{2+} and Zn^{2+} increases the conductivity of the titanates except in the $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ system, where the conductivity decreases slightly at low doping levels, x = 0.01-0.02. The highest conductivity in the $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn) systems is offered by the $(Ln_{0.9}A_{0.1})_2Ti_2O_{7-\delta}$ and attains maximum value for $(Yb_{0.9}Ga_{0.1})_2Ti_2O_{6.9}$ and $(Yb_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$ solid solutions: $\sim 2 \times 10^{-2}$ and 9×10^{-3} S cm⁻¹ at 750 °C, respectively. Ca and Mg are best dopants for $Ln_2Ti_2O_7$ (Ln = Dy, Ho, Yb) pyrochlores. Using impedance spectroscopy data, we have determined the activation energies for bulk and grain-boundary conduction in most of the $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho; A = Ca, Mg, Zn) materials. The values obtained, 0.7–1.05 and 1–1.4 eV, respectively, are typical of oxygen ion conductors. We have also evaluated defect formation energies in the systems studied.

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1. Introduction

A number of oxygen-ion-conducting rare-earth titanate pyrochlores (LANTIOX family) have recently been shown to be good solid electrolytes, some surpassing YSZ in electrical conductivity [1–5]. In particular, Ca doping of Yb₂Ti₂O₇ on the Yb site was found to ensure high conductivity of $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$: $\sim 2 \times 10^{-2}$ S cm⁻¹ at 740 °C and ~ 0.2 S cm⁻¹ at 1000 °C [5].

Among the Ln₂O₃-TiO₂ systems containing pyrochlore-like compounds and solid solutions with high oxygen ion conductivity (LANTIOX), the Ho₂O₃-TiO₂ and Dy₂O₃-TiO₂ systems remain the least explored. By analogy with $(Yb_{1-x}Ca_x)_2Ti_2O_{6.9}$, the highest ionic conductivity in these systems would be expected to result from aliovalent Ln-site substitutions.

Studies aimed at optimizing the concentration of R_2O_3 oxides as acceptor dopants stabilizing the high-temperature, oxygen-ionconducting phase of ZrO_2 have shown that cubic zirconia has the highest conductivity at the lowest possible stabilizer concentrations: 8–11 mol% Y_2O_3 and 9–11 mol% Sc_2O_3 . Higher doping levels reduce its ionic conductivity, promoting oxygen vacancy-dopant association [6]. There is also substantial evidence that the formation of such defect complexes is favoured by considerable size mismatches between the dopant cation and Zr^{4+} [7–11].

Experimental data on doping of $R_2Ti_2O_7$ (R = Y, Sm, Gd) with divalent cations (Mg²⁺, Ca²⁺, Sr²⁺) demonstrate that Ca is the most efficient dopant [12]. According to atomistic simulations [13], Sr-doped pyrochlore oxides have a low Sr'_A– $V_0^{\bullet\bullet}$ binding energy and hence a low activation energy for oxygen migration, which is however in contradiction with experimental data [12]. Mg²⁺ proved the least efficient dopant for $R_2Ti_2O_7$ with R = Y, Sm and Gd [12].

The effect of cation disorder on oxygen transport in the materials in question is still the subject of controversy. Ti_{Ln} anti-site defects may influence the degree of divalent-cation substitution on the lanthanide site [14]. This led us to examine divalent-cation doping of heavy-lanthanide titanates (using $Yb_2Ti_2O_7$ as a model system), which have the strongest tendency toward anti-structure pair formation (cation disordering) [15], and intermediate-lanthanide titanates (Ln = Dy, Ho), in which this tendency is less pronounced.

Our main purposes were to study the effect of Group IIA and IIB $(Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+})$ cation substitutions in the lanthanide

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Table 1

Preparation conditions and	1 phase	composition	of the	samples
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Composition	Sample No.	x	Method and firing conditions	Phase composition
Ho ₂ Ti ₂ O ₇	1	0	Solid-state reaction; 1600 °C, 4 h	Pyrochlore
	2	0	Co-precipitation; 1600 °C, 4 h	Pyrochlore
$(Ho_{1-x}Mg_x)_2Ti_2O_{7-\delta}$	3	0.04	Solid-state reaction; 1600 °C, 4 h	Pyrochlore
	4	0.1	Solid-state reaction; 1600 °C, 4 h	Pyrochlore
$(Ho_{1-x}Zn_x)_2Ti_2O_{7-\delta}$	5	0.04	Solid-state reaction; 1600 °C, 4 h	Pyrochlore
	6	0.07	Solid-state reaction; 1600 °C, 4 h	Pyrochlore
	7	0.1	Solid-state reaction; 1400 °C, 4 h	Solidified melt
$(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$	8	0.01	Co-precipitation; 1400 °C, 4 h	Pyrochlore
	9	0.01	Co-precipitation; 1600 °C, 4 h	Pyrochlore
	10	0.02	Co-precipitation; 1600 °C, 4 h	Pyrochlore
	11	0.04	Co-precipitation; 1400 °C, 4 h	Pyrochlore
	12	0.04	Co-precipitation; 1600 °C, 4 h	Pyrochlore
	13	0.1	Co-precipitation; 1400 °C, 4 h	Pyrochlore
	14	0.1	Co-precipitation; 1600 °C, 4 h	Pyrochlore
Dy ₂ Ti ₂ O ₇	15	0	Solid-state reaction; 1400 °C, 4 h	Pyrochlore + TiO ₂
-	16	0	Solid-state reaction; 1600 °C, 4 h	Pyrochlore
	17	0	Co-precipitation; 1400 °C, 4 h	Pyrochlore
	18	0	Co-precipitation; 1600 °C, 4 h	Pyrochlore
$(Dy_{1-x}Sr_x)_2Ti_2O_{7-\delta}$	19	0.04	Solid-state reaction, 1050 °C, 10 h, 1400 °C, 4 h, 1500 °C, 4 h	Pyrochlore + SrTiO ₃ (tr
	20	0.1		Pyrochlore + SrTiO ₃
	21	0.1	Mechanical activation + firing; 1400 °C, 4 h + 1500 °C, 4 h	Pyrochlore + SrTiO ₃
$(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$	22	0.02	Co-precipitation; 1400 °C, 4 h	Pyrochlore
	23	0.02	Co-precipitation; 1600 °C, 4 h	Pyrochlore
	24	0.04	Solid-state reaction; 1600 °C, 4 h	Pyrochlore
	25	0.04	Co-precipitation; 1400 °C, 4 h	Pyrochlore
	26	0.04	Co-precipitation; 1600 °C, 4 h	Pyrochlore
	27	0.1	Solid-state reaction; 1400 °C, 4 h	Pyrochlore
	28	0.1	Solid-state reaction; 1600 °C, 4 h	Solidified melt
	29	0.1	Mechanical activation + firing; 1400 °C, 4 h	Pyrochlore
	30	0.1	Co-precipitation; 1400 °C, 4 h	Pyrochlore
	31	0.1	Co-precipitation; 1600 °C, 4 h	Pyrochlore
(Yb _{0.9} Ca _{0.1}) ₂ Ti ₂ O _{6.9}	32	0.1	Mechanical activation + firing; 1400 °C, 4 h	Pyrochlore
(Yb _{0.9} Mg _{0.1}) ₂ Ti ₂ O _{6.9}	33	0.1	Mechanical activation + firing; 1400 °C, 4 h	Pyrochlore

sublattice of the Ln₂Ti₂O₇ (Ln = Dy, Ho, Yb) titanate pyrochlores on the total, bulk and grain-boundary conductivities of these solid electrolytes and to establish appropriate dopants for Ln₂Ti₂O₇ (Ln = Dy, Ho, Yb) and optimize conditions for achieving high conductivity in (Ln_{1-x}A_x)₂Ti₂O_{7- δ} (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn) oxygen ion conductors.

2. Experimental

2.1. Synthesis of polycrystalline $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Mg, Ca, Sr, Zn)

A number of samples were prepared by solid-state reactions using as-purchased chemicals: CaCO₃, Sr(NO₃)₂, ZnO, MgO, TiO₂, Dy₂O₃, Ho₂O₃ and Yb₂O₃. Appropriate powder mixtures were ground in acetone and pressed into discs, which were then placed in alundum crucibles and fired in air at 1400–1600 °C for 4–8 h. After firing, all the samples were furnace-cooled (130 °C h⁻¹). The sample compositions and firing temperatures are listed in Table 1.

 $(Ln_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (Ln = Dy, Yb), $(Yb_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$ and $(Dy_{0.9}Sr_{0.1})_2Ti_2O_{6.9}$ were synthesized by firing oxide mixtures mechanically activated in an Aronov eccentric vibratory mill [5,16].

In addition, $(Ln_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho) samples were produced through co-precipitation. The DyCl₃ and HoCl₃ solutions used were prepared by dissolving Dy₂O₃ and Ho₂O₃ in 15% HCl while heating the mixture. The H₂TiCl₆ solution was prepared by dissolving anhydrous TiCl₄ in concentrated HCl. The solution concentrations were determined gravimetrically. An appropriate mixture of the H₂TiCl₆, LnCl₃ and Ca(NO₃)₂ solutions was added dropwise to a vigorously stirred mixture of concentrated aqueous ammonia (50%), concentrated ammonium bicarbonate solution (25%) and water (25%). The precipitate was washed four times with hot water and then centrifuged until the ammonia smell was very weak. After air drying at 100 °C for 24 h, the powder was ground and prefired at 650 °C for 2 h. Next, the powder was pressed into discs, which were sintered in a muffle furnace at 1400 and 1600 °C.

2.2. Characterization techniques

The samples were characterized by X-ray diffraction (XRD) at room temperature and by impedance spectroscopy at temperatures from 300 to 1000 °C and frequencies from 10 mHz to 3 MHz under atmospheric oxygen partial pressure.

2.2.1. XRD examination

Data were collected on a DRON-3 M diffractometer (Cu K α radiation, $\lambda = 1.5418$ Å, Bragg–Brentano geometry, 35 kV, 28 mA, $2\theta = 13-65^{\circ}$, scan step of 0.02° or 0.05°). Phase compositions were determined using JCPDS-ICDD PCPDFWIN v. 2.3 data. In determining lattice parameters and analysing the samples for phase purity, we used WinXPow software and the ICDD PDF database.

2.2.2. Impedance spectroscopy

In electrical measurements, we used disc-shaped polycrystalline samples 6–12 mm in diameter and 1–5 mm in thickness. Contacts to the sample faces were made by firing ChemPur C3605 paste, containing colloidal platinum, at 950–1000 °C. The resistance of the contacts was within several ohms.

Measurements were performed by a two-probe method in the frequency range 10 mHz to 3 MHz at 13 fixed temperatures from 300 to 1000 °C and an applied sinusoidal voltage of 0.5 V peak, using a Novocontrol Beta-N impedance analyser and a NorECs ProboStat ceramic cell fitted with platinum electrodes and a Pt/Pt-Rh thermocouple.

Table 2

Eight-coordinate ionic radii of lanthanides, $R(Ln_{CN-8}^{3+})$, and dopants, $R(A_{CN-8}^{2+})$, and the lanthanide–dopant size mismatch ΔR in some of the $(Ln_{0.9}A_{0.1})_2$ Ti₂O_{6.9} (Ln = Dy, Ho, Yb; A = Mg, Ca, Sr, Zn) solid solutions studied.

Composition	$R(Ln_{CN=8}^{3+})(Å)$ [19]	$R(A_{CN=8}^{2+})$ [19]	ΔR (Å)
(Yb _{0.9} Ca _{0.1}) ₂ Ti ₂ O _{6.9}	Yb, 0.985	Ca, 1.12	0.135
(Dy _{0.9} Ca _{0.1}) ₂ Ti ₂ O _{6.9}	Dy, 1.027	Ca, 1.12	0.093
(Yb _{0.9} Mg _{0.1}) ₂ Ti ₂ O _{6.9}	Yb, 0.985	Mg, 0.89	0.095
(Ho _{0.9} Ca _{0.1}) ₂ Ti ₂ O _{6.9}	Ho, 1.015	Ca, 1.12	0.105
(Dy _{0.9} Sr _{0.1}) ₂ Ti ₂ O _{6.9}	Dy, 1.027	Sr, 1.26	0.233
(Ho _{0.9} Zn _{0.1}) ₂ Ti ₂ O _{6.9}	Ho, 1.015	Zn, 0.9	0.115
$(Ho_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$	Ho, 1.015	Mg, 0.89	0.125

3. Results and discussion

3.1. Structure evolution of $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (*Ln* = *Dy*, *Ho*, *Yb*; *A* = *Ca*, *Mg*, *Zn*; *x* = 0–0.1)

All our samples (Table 1) had a pyrochlore-like structure. Fig. 1 shows plots of the lattice parameter versus dopant concentration for the seven series of samples studied. These data demonstrate that, for $x \le 0.04$, the incorporation of Ca²⁺, the largest dopant cation (Table 2), into the lanthanide (Dy, Ho, Yb) sublattice increases the lattice parameter (Fig. 1a), except for the $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ series prepared via co-precipitation followed by firing at 1400 °C (Fig. 1b). At higher Ca contents, the lattice parameter increases in the $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (x = 0, 0.05, 0.1) (Fig. 1a, curve 1), $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (x = 0, 0.02, 0.04, 0.1) (Fig. 1a, curve 3) and $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (Fig. 1b, curve 4) systems and varies very little in the $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ series from x = 0.04 to x = 0.1 (Fig. 1b, curve 3). $(Ho_{0.99}Ca_{0.01})_2Ti_2O_{7-\delta}$ sample shows the lowest parameter in this series.



Fig. 1. Lattice parameter as a function of dopant concentration for the solid solutions studied: (a) (1) $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (mechanical activation, firing at 1400 °C), (2) $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (co-precipitation, firing at 1400 °C), (3) $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (co-precipitation, firing at 1600 °C), (3) $(Ho_{1-x}Za_x)_2Ti_2O_{7-\delta}$ (solid-state reaction at 1600 °C), (2) $(Ho_{1-x}Mg_x)_2Ti_2O_{7-\delta}$ (solid-state reaction at 1600 °C), (2) $(Ho_{1-x}Mg_x)_2Ti_2O_{7-\delta}$ (solid-state reaction, firing at 1400 °C), (2) $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (solid-state reaction, firing at 1400 °C), (2) $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (solid-state reaction, firing at 1400 °C), (3) $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (solid-state reaction, firing at 1600 °C).

Doping with Zn and Mg (Fig. 1b, curves 1 and 2), which have markedly smaller ionic radii, reduces the lattice parameter for $x \le 0.07$ in the $(Ho_{1-x}Zn_x)_2Ti_2O_{7-\delta}$ system and for $x \le 0.04$ in $(Ho_{1-x}Mg_x)_2Ti_2O_{7-\delta}$. At Mg contents above x = 0.04, the lattice parameter remains constant to within experimental uncertainty.

3.2. Analysis of impedance spectra

Fig. 2a–d shows the impedance spectra of four different samples obtained in this study. The spectra are well resolved, which enables the bulk (intragranular), grain-boundary and electrode components of conductivity to be separately assessed (Fig. 3).

For all the samples, independent on the preparation method, the semicircles in the impedance spectra are better resolved at low temperatures than at high temperatures (T > 700 °C). The reason for this is that, with increasing temperature and diffusion rate, the properties of grain boundaries approach those of the bulk because of the rise in conductivity.

The present impedance data are well represented by the frequency response of the equivalent circuit proposed by Boukamp [17] for solid electrolytes (Fig. 4, Table 3), which comprises three (occasionally two) series connected elements, each composed of a parallel connected resistor and constant phase element (with an impedance $Z = 1/a(i\omega)^{b}$, where 0 < b < 1). This provides indirect evidence that the conduction in the materials studied is predominantly ionic.

3.3.3. Acceptor doping $Yb_2Ti_2O_7$ with Ca and Mg: $(Yb_{1-x}A_x)_2Ti_2O_{7-\delta}$ (A = Ca, Mg; x = 0.1)

3.3.1. Acceptor doping $Dy_2Ti_2O_7$ with Ca and Sr: $(Dy_{1-x}A_x)_2Ti_2O_{7-\delta}$ (A = Ca, Sr; x = 0, 0.02, 0.04, 0.1)

Fig. 5 shows Arrhenius plots of total, bulk and grain-boundary conductivities for $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ synthesized via co-precipitation followed by firing at 1600 °C. The conductivity of the doped materials for the most part exceeds that of $Dy_2Ti_2O_7$, which lends support to a vacancy mechanism of conduction in the $Ln_2Ti_2O_7$ pyrochlores [12]. Note that the conductivity rises markedly at low doping levels, with a much more gradual increase at x near 0.1. Similar behaviour was reported for other oxygen ion conductors [18]. The total high-temperature conductivity is seen to slightly increase as the synthesis temperature changes from 1400 to 1600 °C (Fig. 6). Only at low temperatures and high doping levels does the opposite relationship hold, as illustrated by the conductivity-composition-temperature diagram in Fig. 6.

Fig. 7 shows Arrhenius plots of conductivity for Ca- and Srsubstituted $Dy_2Ti_2O_7$ prepared by solid-state reactions. The conductivity of $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ increases with Ca content, while $(Dy_{0.96}Sr_{0.04})_2Ti_2O_{6.96}$, which was found to contain trace levels of SrTiO₃, is close in conductivity to undoped $Dy_2Ti_2O_7$.

The data in Fig. 8 demonstrate that the conductivity of the $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ samples prepared via co-precipitation and



Fig. 2. (a) Impedance spectra of sample 18 (Dy₂Ti₂O₇, co-precipitation). (b) Impedance spectra of sample 14 ((Ho_{0.9}Ca_{0.1})₂Ti₂O_{6.9}, co-precipitation). (c) Impedance spectra of sample 29 ((Dy_{0.9}Ca_{0.1})₂Ti₂O_{6.9}, mechanically activated starting mixture). (d) Impedance spectra of sample 27 ((Dy_{0.9}Ca_{0.1})₂Ti₂O_{6.9}, solid-state reaction).



Fig. 3. Evaluation of different contributions to total conductivity as exemplified by the 400 °C impedance spectrum of sample 19 ((Dy_{0.96}Sr_{0.04})₂Ti₂O_{6.96}).

Table 3 Equivalent circuit parameters for $(Ho_{0.96}Zn_{0.04})_2Ti_2O_{6.96}$ (see Fig. 4).

Parameter	Value (Ω)	Parameter	Value (F)	Parameter	Value
R1	$\textbf{2.83}\times 10^{5}$	CPE1-T	1.22×10^{-11}	CPE1-P	0.95
R2	2.16×10^5	CPE2-T	$2.16 imes10^{-8}$	CPE2-P	0.76
R3	$\textbf{2.13}\times 10^6$	CPE3-T	1.31×10^{-6}	CPE3-P	0.50



Fig. 4. 400 °C impedance spectrum of sample 5 ($(Ho_{0.96}Zn_{0.04})_2Ti_2O_{6.96}$) and equivalent circuit fit. $Z_{CPE} = 1/T(i\omega)^p$ (the equivalent circuit parameters are listed in Table 3).

from mechanically activated oxides (Table 1, sample Nos. 22 and 29) is a factor of 5 higher than that of the $x_{Ca} = 0.1$ material prepared by solid-state reaction at the same temperature (1400 °C) (Table 1 sample No. 27). It seems likely that the first two procedures ensure a more even dopant distribution over the



Fig. 5. Arrhenius plots of total, bulk and grain-boundary conductivities for $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ prepared via co-precipitation followed by firing at 1600 °C (samples 18, 23, 26, 31).

ceramic grains. The data for the samples prepared by solid-state reactions exhibit deviations from Arrhenius behaviour (Fig. 7): their grain-boundary conductivity is a stronger function of temperature compared to the Arrhenius equation. One possible reason for this is the presence of an intergranular amorphous phase, which cannot be detected by XRD.

3.3.2. Acceptor doping Ho₂Ti₂O₇ with Ca, Mg and Zn: (Ho_{1-x}A_x)₂Ti₂O_{7- δ} (A = Ca, Mg, Zn; x = 0, 0.02, 0.04, 0.1)

Fig. 9 shows Arrhenius plots of total, bulk and grain-boundary conductivities for $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ synthesized via co-precipitation followed by firing at 1600 °C. The behaviour of conductivity differs somewhat from that in the Dy system. At low doping levels (x = 0.01-0.02), the conductivity of $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ is below



Fig. 6. Conductivity-composition-temperature diagram for the $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ samples prepared via co-precipitation followed by firing at 1400 and 1600 °C.



Fig. 7. Arrhenius plots of total, bulk and grain-boundary conductivities for $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ and $(Dy_{1-x}Sr_x)_2Ti_2O_{7-\delta}$ prepared by solid-state reactions at 1500–1600 °C (samples 16, 19, 24, 28).

that of $Ho_2Ti_2O_7$ (Fig. 9), primarily because of the increase in the resistance of the intergranular phase.

In the range x = 0.04-0.1, the conductivity of the pyrochlorelike $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ increases with Ca content like in $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (x = 0-0.1) samples. The bulk and grainboundary components of conductivity in these materials (Fig. 9) show insignificant deviations from Arrhenius behaviour. Together with the observed activation energies, typical of oxygen ion conductors (Table 4), the Arrhenius behaviour points to predominantly ionic conduction in the solid solutions studied.

Fig. 10 shows Arrhenius plots of total, bulk and grain-boundary conductivities for $(Ho_{1-x}Mg_x)_2Ti_2O_{7-\delta}$ (x = 0, 0.04, 0.07, 0.1) and $(Ho_{1-x}Zn_x)_2Ti_2O_{7-\delta}$ (x = 0, 0.04, 0.07) prepared by solid-state reactions at 1600 °C. The conductivity of $(Ho_{1-x}A_x)_2Ti_2O_{7-\delta}$ (A = Mg, Zn; x = 0-0.1) increases with dopant (A = Mg, Zn) content like in the $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (x = 0.04-0.1) series. Clearly, Mg is better dopant then Zn. The total and bulk conductivities are seen to exhibit nearly Arrhenius behaviour, whereas the grain-boundary



Fig. 8. Arrhenius plots of bulk conductivity for $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ synthesized at 1400 °C using (1) mechanical activation, (2) co-precipitation and (3) solid-state reaction.



Fig. 9. Arrhenius plots of total, bulk and grain-boundary conductivities for $(Ho_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ prepared via co-precipitation followed by firing at 1600 °C (samples 2, 9, 10, 12, 14).



Fig. 10. Arrhenius plots of total, bulk and grain-boundary conductivities for $(Ho_{1-x}Mg_x)_2Ti_2O_{7-\delta}$ and $(Ho_{1-x}Zn_x)_2Ti_2O_{7-\delta}$ prepared by solid-state reactions at 1600 °C (samples 1, 3–6).

Table 4

Activation energy for oxygen hopping (E_a') and the difference between the activation energy for ionic conduction and that for oxygen hopping (g) in some of the materials studied.

Sample No.	Composition	E_{a}' (eV)	g (eV)
1	Ho ₂ Ti ₂ O ₇	0.78	0.19
3	(Ho _{0.96} Mg _{0.04}) ₂ Ti ₂ O _{6.96}	0.85	0.11
4	(Ho _{0.9} Mg _{0.1}) ₂ Ti ₂ O _{6.9}	0.88	0.14
5	(Ho _{0.96} Zn _{0.04}) ₂ Ti ₂ O _{6.96}	0.77	0.16
6	(Ho _{0.93} Zn _{0.07}) ₂ Ti ₂ O _{6.93}	0.74	0.22
16	Dy ₂ Ti ₂ O ₇	0.75	0.23
18	Dy ₂ Ti ₂ O ₇	0.69	0.18
23	(Dy _{0.98} Ca _{0.02}) ₂ Ti ₂ O _{6.98}	0.83	0.12
26	(Dy _{0.96} Ca _{0.04}) ₂ Ti ₂ O _{6.96}	0.88	0.07
31	(Dy _{0.9} Ca _{0.1}) ₂ Ti ₂ O _{6.9}	0.87	0.12
2	Ho ₂ Ti ₂ O ₇	0.75	0.19
9	(Ho _{0.99} Ca _{0.01}) ₂ Ti ₂ O _{6.99}	0.80	0.10
10	(Ho _{0.98} Ca _{0.02}) ₂ Ti ₂ O _{6.98}	0.77	0.18
12	(Ho _{0.96} Ca _{0.04}) ₂ Ti ₂ O _{6.96}	0.76	0.21
14	(Ho _{0.9} Ca _{0.1}) ₂ Ti ₂ O _{6.9}	0.83	0.18



Fig. 11. Arrhenius plots of bulk conductivity for (1) $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$, (2) $(Yb_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$, (3) $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1600 °C), (4) $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1400 °C), (5) $(Ho_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1600 °C), (6) $(Ho_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1400 °C), (7) $(Ho_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$ (solid-state reaction, 1600 °C) and (8) $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$

component is a stronger function of temperature. Such behaviour of grain-boundary conductivity, very typical of ceramics produced by solid-state reactions, suggests the presence of an intergranular amorphous phase, like in $(Dy_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ prepared by solid-state reactions.

3.3.3. Acceptor doping $Yb_2Ti_2O_7$ with Ca and Mg: $(Yb_{1-x}A_x)_2Ti_2O_{7-\delta}$ (A = Ca, Mg; x = 0.1)

Fig. 11 shows Arrhenius plots of bulk conductivity for $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (Fig. 11, curve 1) and $(Yb_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$ (Fig. 11, curve 2) prepared using mechanical activation at 1400 °C. The conductivity of Ca-doped sample is higher then Mg-doped.

3.3.4. Lanthanide effect on the conductivity of titanates

 $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Ca, Mg; x = 0.1). Comparative study

In this study, following Kramer et al. [12] we used divalent dopants: Mg, Ca, Sr (Group IIA) and Zn (Group IIB).

We failed to obtain phase-pure $(Dy_{0.9}Sr_{0.1})_2Ti_2O_{6.9}$ by any of the procedures used (Table 1), probably because of the large ionic radius of Sr^{2+} (for CN = 8: Sr^{2+} , 1.26 Å; Ca^{2+} , 1.12 Å; Dy^{3+} , 1.027 Å [19]). $(Dy_{0.96}Sr_{0.04})_2Ti_2O_{6.96}$ also contained $SrTiO_3$ (trace levels).

In an earlier study of $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}(x = 0, 0.05, 0.1)$ [5], the highest conductivity was achieved at x = 0.1. Fig. 11 compares the bulk conductivity data for most of the $(Ln_{0.9}A_{0.1})_2Ti_2O_{6.9}$ (A = Ca, Mg) samples synthesized in this work. The data in Fig. 8 demonstrate that the $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ ceramics prepared via mechanical activation and co-precipitation, followed by firing at the same temperature are close in conductivity. Therefore, the conductivity data for materials prepared by these procedures can be analysed together. The highest conductivity is offered by $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (Fig. 11, curve 1). The 750 °C bulk conductivity of $(Yb_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$, $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$, $(Ho_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ is close to each other (Fig. 11, curves 2-5). It is interesting that conductivity of $(Ho_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$, synthesized at 1600 °C from oxides mixture using solid-state method (Fig. 11, curve 7) is close to the bulk conductivity of $(Yb_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$, $(Dy_{0.9}Ca_{0.1})_2$ Ti₂O_{6.9}, (Ho_{0.9}Ca_{0.1})₂Ti₂O_{6.9} prepared at lower temperature (1400 °C) using more homogeneous techniques (mechanical activation and co-precipitation) (Fig. 11, curves 2, 4, 5). At first we have supposed that the highest conductivity of Yb- and Dy-contained samples is related to the presence of Dy and Yb in two oxidation states 2+ and 3+, whereas Ho is known to have only one oxidation state. But according to data presented at Fig. 11 the bulk conductivity of $(Ho_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1600 °C), (Fig. 11, curve 5) is practically the same as for $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1600 °C) (Fig. 11, curve 3).

3.4. Conduction mechanism in pyrochlore-like $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn)

The present conductivity versus frequency and temperature data can be used to evaluate the activation energy for oxygen hopping (E_a') and the difference between the activation energy for ionic conduction (E_a) and that for oxygen hopping ($g = E_a - E_a'$) in the ($Ln_{1-x}A_x$)₂Ti₂O_{7- δ} (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn) solid electrolytes.

As shown by Almond and West [20], the real part of conductivity can, to some approximation, be written in the form Re $\sigma(\omega) = \sigma_{dc}(1+(\omega/\omega_h)^{\gamma})$, where σ_{dc} is the dc conductivity, and ω and ω_h are the angular frequencies of the applied field and ion hopping, respectively. If the part of an impedance spectrum corresponding to bulk conduction can be fitted with the frequency response of an equivalent circuit composed of a parallel connected resistor and constant phase element, ω_h can be expressed through the parameters of the circuit: $\omega_h = (Ra \cos(b\pi/2))^{-1/b}$, where *R* is the resistance, and *a* and *b* are the parameters of the constant phase element (with an impedance $Z = 1/a(i\omega)^b$) (Table 3).

From $\omega_{\rm h}(T)$ data, one can easily evaluate the activation energy for hopping, $E_{\rm a'}$, using the equation $\omega_{\rm h} = \omega_0 \exp(-E_{\rm a'}/KT)$, which gives a linear relation between $\log \omega_{\rm h}$ and T^{-1} . The results for some of our samples are presented in Table 4. A literature search revealed no data that could be used to assess the accuracy of these estimates.

On the whole, the data in Table 4 are consistent with the notion that acceptor doping in the cation sublattice reduces the formation energy of oxygen vacancies, thereby raising their concentration compared to the unsubstituted titanates.

4. Conclusions

 $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho; A = Ca, Mg, Zn; x = 0–0.1) pyrochlore solid solutions have been prepared for the first time using mechanical activation, co-precipitation and solid-state reactions.

Based on the present impedance spectroscopy data, Arrhenius plots of conductivity, and activation energies, we proposed an oxygen vacancy mechanism of conduction in the($Ln_{1-x}A_x$)₂Ti₂O_{7- δ} (Ln = Dy, Ho; A = Ca, Mg, Zn; x = 0-0.1) pyrochlore-like ceramics and revealed basic trends in their oxygen ion conductivity as a function of composition and temperature.

The conductivity of $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn) increases mainly with A^{2+} content in the range x = 0-0.1 and attains the maximum value for x = 0.1.

The bulk high-temperature conductivity of $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn) series increases with reduction of the Ln radius.

The highest conductivity in the $(Ln_{1-x}A_x)_2Ti_2O_{7-\delta}$ (Ln = Dy, Ho, Yb; A = Ca, Mg, Zn) systems is offered by $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$. The conductions of $(Yb_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$, $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (mechanical activation, 1400 °C), $(Ho_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1400 and 1600 °C), $(Dy_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ (co-precipitation, 1600 °C) are close to each other. The conductivity of $(Ho_{0.9}Mg_{0.1})_2Ti_2O_{6.9}$, synthesized by solid-state reaction at 1600 °C, is slightly lower. Ca and Mg are the best dopants for $Ln_2Ti_2O_7$ (Ln = Dy, Ho, Yb).

The conductivity of the ceramics prepared via co-precipitation and from mechanically activated oxides exceeds that of the samples prepared by solid-state reactions at the same temperature, owing to a more even dopant distribution over the ceramic grains. The solid-state method can, in principle, provide the close doping distribution but only at the higher synthesis temperatures. However the grain-boundary conductivity component is seen to have non-Arrhenius behaviour in the samples synthesized by solid-state method.

The activation energy for conduction depends little on the sample composition and preparation procedure, with a tendency to rise upon A^{2+} substitution for Ln^{3+} .

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