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Mixed conductivity of garnet phases based on gadolinium ferrite

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Abstract

Incorporation of Pr and Ca into the garnet lattice of $Gd_3Fe_5O_{12\pm\delta}$ was found to increase the electronic conductivity, and to decrease the thermal expansion coefficients and oxygen ion transference numbers. The ionic conductivity of $Gd_{2.2}Pr_{0.8}Fe_5O_{12\pm\delta}$ ceramics is similar to that of undoped gadolinium ferrite, whilst $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ exhibits slightly higher ionic transport, suggesting an enhanced vacancy contribution. The activation energies for ionic conduction in $Gd_3Fe_5O_{12}$-based materials vary in the narrow range 211–224 kJ/mol. Due to a significantly lower activation energy for the total conductivity (24–81 kJ/mol), the oxygen ion transference numbers in air increase with temperature, from $4 \times 10^{-5} - 5\times10^{-3}$. Steady-state oxygen permeation fluxes through dense garnet membranes are limited by bulk ambipolar conductivity. The thermal expansion coefficients of the ferrite ceramics (100–1000 °C) were found linear and in the range $10.36–10.86 \times 10^{-6}$ K^{-1}.

Keywords: Ferrites; Garnets; Ionic conductivity; Membranes; Thermal expansion

1. Introduction

Oxide ceramics with mixed ionic-electronic conductivity are vital for numerous electrochemical applications, including ceramic membranes for oxygen separation and partial oxidation of hydrocarbons. However, most known mixed conductors possess significant disadvantages. In particular, perovskite-type oxides with high oxygen permeability are often thermodynamically and/or dimensionally unstable under large oxygen chemical potential gradients, react with gas species such as CO_2 and show very high thermal and chemically-induced expansion.[1] Fluorite-type mixed conductors exhibit, as a rule, low oxygen permeability due to poor electronic conductivity.[1]

This work presents results on the oxygen permeability and ionic conductivity of ferrite garnet ceramics based on $Gd_3Fe_5O_{12}$. Due to unique optical, mechanical and electromagnetic properties, garnet-based materials are frequently used in lasers and phosphorescent sources, and as materials for electronic and ultra-high frequency applications.[2–4] With well-developed processing technologies already available, it is possible and easy to extend their application to other domains. Many rare-earth garnets possess high thermodynamic stability and likely dimensional stability,[2] which may be advantageous for high-temperature electrochemical applications. However, information on oxygen ionic transport in garnet ferrites is scarce.

2. Experimental

A standard solid-state synthesis technique, starting from high-purity metal nitrates and oxides, was used to prepare samples of $Gd_3Fe_5O_{12}$, $Gd_{2.2}Pr_{0.8}Fe_5O_{12}$ and $Gd_{2.5}Ca_{0.5}Fe_5O_{12}$, having 97–99% density. The final reaction stages were carried out at 1000–1420 °C for 10–50 h with intermediate grinding steps until X-ray diffraction (XRD) demonstrated formation of single garnet-type phases. Gas-tight ceramics were uniaxially pressed at 280 –350 MPa as bars ($4 \times 4 \times 30$ mm^3) and disks of various thicknesses (diameter 12–15 mm) and then fired in air for 5 h; the sintering temperatures (Table 1) were selected on the basis of experimental data on the density vs. sintering conditions. One additional series of $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ samples was sintered for 50 hours in order to obtain ceramics with large grain size. XRD and picnometric measurements showed no significant changes in the crystal lattice and density after the prolonged thermal treatment. Before characterization, all ceramic samples were annealed in air at 900–1000 °C for 5–10 h and then slowly cooled (2–3 K/min) for equilibration with the atmosphere at low tempera-

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Table 1
Properties of $Gd_3Fe_5O_{12}$-based ceramics

Composition	Sintering temperature, °C	Unit cell parameter a,nm	Average TEC $\alpha\times10^6$, K^{-1} (100-1000 °C)	Relative density ρ_{exp}/ρ_{theor},%
$Gd_3Fe_5O_{12}$	1470	1.2474	10.86±0.01	99.3
$Gd_{2.2}Pr_{0.8}Fe_5O_{12}$	1420	1.2503	10.76±0.01	98.0
$Gd_{2.5}Ca_{0.5}Fe_5O_{12}$	1220	1.2459	10.36±0.01	97.4

	Activation energy*, kJ/mol		Oxygen ion transference numbers		
	Total conductivity	Ionic transport	900 °C	950 °C	1000 °C
$Gd_3Fe_5O_{12}$	81±1	214±11	1.7×10^{-3}	3.1×10^{-3}	4.7×10^{-3}
$Gd_{2.2}Pr_{0.8}Fe_5O_{12}$	32.6±0.6	224±14	3.6×10^{-4}	8.9×10^{-4}	1.6×10^{-3}
$Gd_{2.5}Ca_{0.5}Fe_5O_{12}$	23.7±0.1	211±12	3.9×10^{-5}	9.4×10^{-5}	1.7×10^{-4}

Note: the activation energy values for the total and ionic conductivity correspond to the temperature ranges 500–1000 and 900–1000 °C, respectively.

tures. The materials were characterized by XRD, scanning electron microscopy combined with energy dispersive spectroscopy (SEM/EDS), dilatometry, 4-probe DC conductivity and steady-state oxygen permeability measurements. The experimental procedure was reported elsewhere.[5–7] All data on oxygen permeability presented in this paper corresponds to a membrane feed-side oxygen partial pressure (p_2) of 21 kPa (air); the thickness of ceramic membranes (d) varied from 0.60 to 1.40 mm.

3. Results and discussion

XRD analysis showed that all $Gd_{3-x}A_xFe_5O_{12}$ ceramics are single-phase and possess a cubic garnet-type structure (space group $Ia\bar{3}d$); the lattice parameters are listed in Table 1. The unit cell volume was found to increase when Pr cations, larger than the host Gd, are incorporated in the A-site sublattice. Doping with Ca leads to a cell contraction, which may be associated with increasing average oxidation state of Fe ions and, thus, decreasing size. However, the garnet structure is quite complex, consisting of 160 atoms that are not close packed. Thus, direct correlations between lattice volume and ionic sizes may be oversimplified.

SEM micrographs showing $Gd_{3-x}A_xFe_5O_{12\pm\delta}$ ceramics are presented in Fig. 1. The grain size was found to be primarily dependent on the sintering temperature, which increases from 1220 °C for $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ up to 1420–1470 °C in the case of $Gd_{2.2}Pr_{0.8}Fe_5O_{12\pm\delta}$ and $Gd_3Fe_5O_{12\pm\delta}$ (Table 1). This is accompanied with an increase in the average grain size from 2–5 μm for Ca-containing material, to 7–15 μm for the two latter compositions.

The thermal expansion of garnet ferrites is almost linear, indicating an absence of phase changes. The average thermal expansion coefficients (TECs) vary in the relatively narrow range 10.3 – 10.9 × 10^{-6} K^{-1}, slightly decreasing on doping (Table 1). As expected, the difference in grain size of $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ ceramics sintered for different periods of time has no effect on the thermal expansion.

The temperature dependence of the conductivity of $Gd_{3-x}A_xFe_5O_{12\pm\delta}$ (Fig. 2), shows that the partial ionic and electronic conductivities increase when Gd^{3+} is replaced by Ca^{2+}, following the trend observed for many perovskite-type phases.[8] Therefore, charge compensation for acceptor-doped $Gd_3Fe_5O_{12}$ may occur via formation of electron holes localized in iron-sites (Fe^{4+}) and oxygen vacancies.

The activation energy for hole conduction (E_a), calculated by the usual Arrhenius equation, is about 80 kJ/mol for undoped $Gd_3Fe_5O_{12\pm\delta}$ and decreases to 25 kJ/mol for $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ (Table 1). Again, this range of E_a values is common for oxide semiconductors with a small-polaron conduction mechanism.[4,8] For the Pr-containing composition, relatively high σ values most likely result from the contribution of variable–valence praseodymium cations (Pr^{3+}/Pr^{4+}) to the conductivity. The formation of a small fraction of Pr^{4+} in the lattice may be compensated by the presence of hyperstoichiometric oxygen. However, as the ionic conductivity of the Pr-doped material is about the same as for the undoped garnet, the mobility of oxygen interstitials must be negligible.

To try to reveal a possible influence of surface exchange on oxygen permeation, Fig. 3 presents the dependencies of the oxygen flux density and specific oxygen permeability, $J(O_2)$, on the oxygen partial pressure gradient for two $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ membranes with different thickness. The quantity $J(O_2)$ is defined as[7]

$$j = \frac{J(O_2)}{d} \cdot \ln\left(\frac{p_2}{p_1}\right) \tag{1}$$

where p_1 is the oxygen partial pressure at the membrane permeate side ($p_2 > p_1$). The permeation fluxes decrease with increasing membrane thickness (Fig. 3A), whilst the specific permeability is thickness-independent (Fig. 3B). As $J(O_2)$ is proportional to $j \times d$, this behavior unambiguously indicates that the effect of oxygen surface exchange on the overall oxygen transport is negligible. Otherwise, the oxygen permeability should increase with increasing membrane thickness due to a decreasing role of surface exchange on the "membrane/gas" boundary. Since the permeation is limited by the membrane bulk transport, $J(O_2)$ is proportional to the so-called ambipolar conductivity (σ_{amb}), averaged for a given oxygen partial pressure range:

$$J(O_2) = \frac{RT}{16F^2} \cdot \overline{\sigma_{amb}} = \frac{RT}{16F^2} \cdot \overline{\sigma t_o(1 - t_o)} \qquad (2)$$

where t_o is the oxygen ion transference number. The values of the ion transference numbers and ionic conductivity, presented in Table 1 and Fig. 2, were calculated using (2) and permeation data obtained with oxygen pressure gradients as small as possible. One should also note that bulk-limited oxygen permeation is found in many perovskite-type ferrites with relatively low ionic conductivity.[5,6]

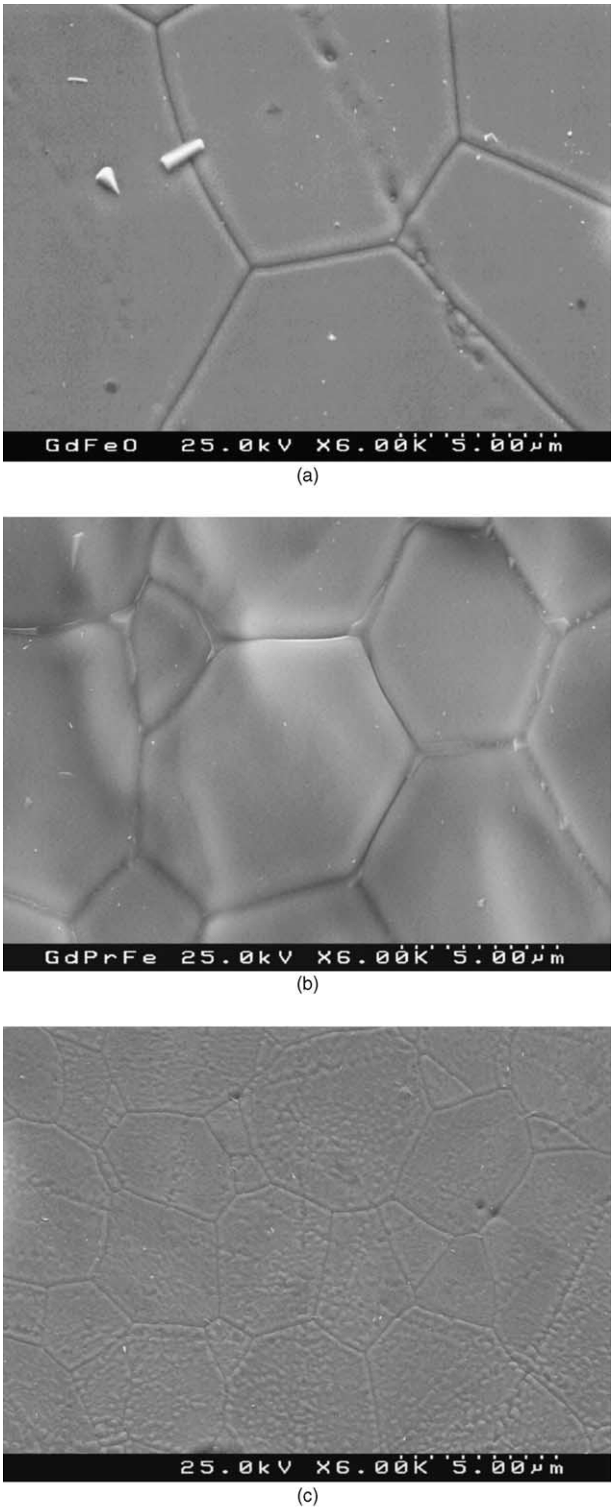

Fig. 1. SEM micrographs of garnet ceramics: $Gd_3Fe_5O_{12}$ (**A**), $Gd_{2.2}Pr_{0.8}Fe_5O_{12}$ (**B**), and $Gd_{2.5}Ca_{0.5}Fe_5O_{12}$ (**C**).

The highest oxygen ionic conductivity was found for the acceptor-doped composition, $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$. Such behavior is in excellent agreement with the literature[4] showing that the ionic transport in garnet-type aluminates occurs via a vacancy mechanism. With respect to aluminate- and gallate-based garnets, even

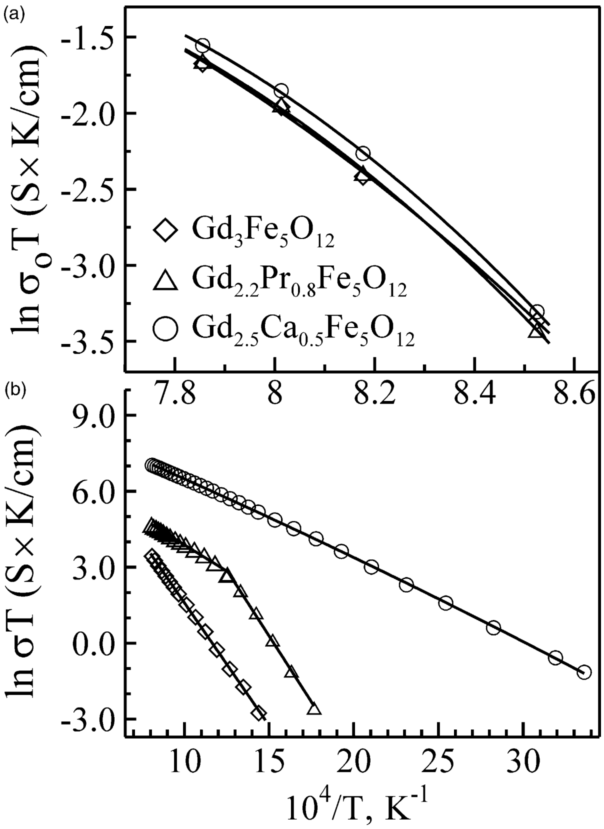

Fig. 2. Temperature dependence of the oxygen ionic (**A**) and total (**B**) conductivities of garnet-type ferrites in air.

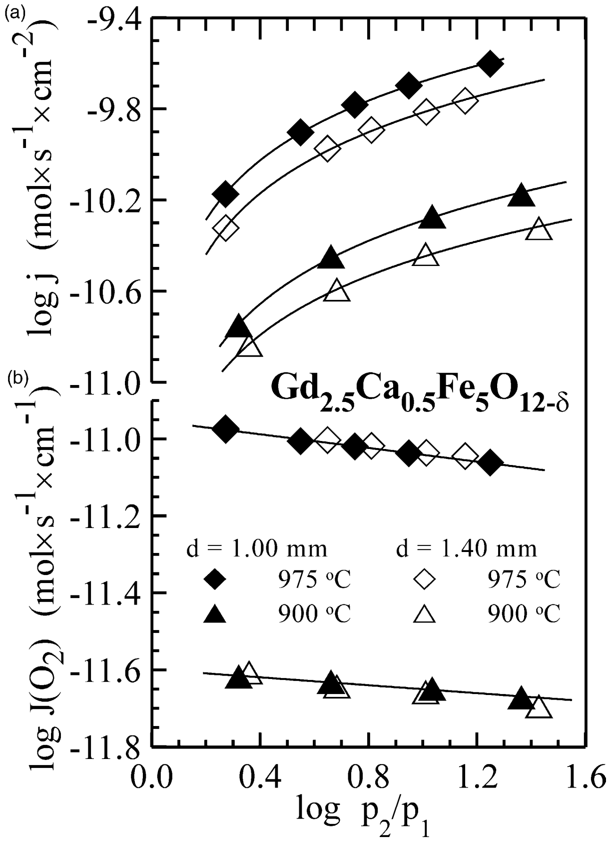

Fig. 3. Oxygen permeation fluxes (**A**) and specific oxygen permeability (**B**) of $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ membranes with different thickness.

the ionic conductivity of undoped $Gd_3Fe_5O_{12}$ is significantly higher.

The activation energy for ionic conduction, in the range 211–224 kJ/mol, is considerably higher than that for electronic transport (Table 1). As a result, the ion transference numbers of garnet ceramics increase when temperature increases. For comparison, the activation energy values for $Y_3Al_5O_{12}$ and $Gd_3Ga_5O_{12}$ are 260–280 kJ/mol.[4,9] While for undoped garnets such difference might be due to a lower energy for oxygen vacancy formation in the ferrite lattice, for Ca-doped materials the activation energy for ionic conduction is certainly determined by the energy required for defect migration.

Lastly, dopant concentrations now used are close to the solubility limits. Attempts to produce $Gd_{3-x}Ca_xFe_5O_{12-\delta}$ solid solutions with x = 0.7–1.0 and $Gd_2PrFe_5O_{12\pm\delta}$ failed. Hence, the possibility for further optimization of $Gd_3Fe_5O_{12}$-based materials seems quite limited.

4. Conclusions

Substitution of gadolinium with praseodymium and calcium in $Gd_3Fe_5O_{12\pm\delta}$ was found to significantly increase the total conductivity, predominantly electronic, and to decrease the activation energy from 81 kJ/mol, for the undoped ferrite, down to 33 and 24 kJ/mol for Pr- and Ca-containing compositions, respectively. The effect of doping on ionic transport is considerably weaker. While the ionic conduction in $Gd_{2.2}Pr_{0.8}Fe_5O_{12\pm\delta}$ is similar to that in undoped $Gd_3Fe_5O_{12\pm\delta}$, the oxygen ionic conductivity of $Gd_{2.5}Ca_{0.5}Fe_5O_{12-\delta}$ ceramics is 5–15% higher, suggesting an enhanced vacancy contribution. The activation energy for ionic transport in ferrite garnets is in the narrow range 211–224 kJ/mol, while the oxygen ion transference numbers vary from 3.9×10^{-5} to 4.7×10^{-3}, increasing with temperature. Oxygen permeation fluxes through garnet membranes are limited by bulk ambipolar conductivity. The thermal expansion coefficients of $Gd_3Fe_5O_{12}$-based ceramics, $10.36–10.86\times10^{-6}$ K^{-1}, are compatible with TECs of solid electrolytes commonly used in high-temperature electrochemical applications.

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