



Antiferroelectric phase transition in pyrochlore-like $(\text{Dy}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_{7-\delta}$ ($x = 0, 0.1$) high temperature conductors

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ABSTRACT

Low-temperature ordering transitions in polycrystalline high temperature conductors $(\text{Dy}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_{7-\delta}$ ($x = 0, 0.1$) prepared using co-precipitation, mechanical activation and solid-state reactions at 1400 or 1600 °C have been studied by impedance spectroscopy at low frequencies and thermal mechanical analysis (TMA). The dielectric permittivity and loss tangent of the ceramics obtained have been measured as a function of temperature at low frequencies (0.5–500 Hz). The results provide evidence for the relaxation of point defects, most likely oxygen vacancies, at 500–600 °C and an antiferroelectric low-temperature phase transition of the second order, associated with re-arrangement process in the oxygen sublattice of pyrochlore structure. The temperature of the antiferroelectric transition is 700 to 800 °C, depending on the synthesis procedure and ceramic composition. Calcium doping of $\text{Dy}_2\text{Ti}_2\text{O}_7$ leads to the formation of additional oxygen vacancies and, in the case of the samples prepared via co-precipitation, increases the peaks in permittivity due to the relaxation process and ordering transition by three or six times, respectively.

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1. Introduction

ZrO_2 stabilized with 8–12 mol% Y_2O_3 or Sc_2O_3 is widely used as a solid electrolyte in high-temperature fuel cells owing to its high oxygen ion conductivity, $\sim 0.1 \text{ S cm}^{-1}$ at 1000 °C. These materials, however, degrade when used at high temperatures, which leads to a drop in their ionic conductivity [1–3]. In studies of polycrystalline Y_2O_3 - and Sc_2O_3 -stabilized (8–12 and 9–12 mol%, respectively) ZrO_2 electrolytes, their ageing (degradation) was assumed to be caused by ordering processes associated with cation diffusion (above 700 °C) and/or by phase transitions due to the high oxygen mobility in these materials [4]. In both systems, the temperature dependences of mechanical and dielectric losses and dielectric permittivity show features due to local jumps of oxygen vacancies, which form electric dipoles with Y or Sc ions around 230 °C [5,6]. In addition, there are a rhombohedral-to-cubic phase transition at 477 °C in the ZrO_2 – Sc_2O_3 system [4,7] and an order–disorder transition at 1177 °C in ZrO_2 stabilized with 12 mol% Y_2O_3 [4,8]. All the polycrystalline materials studied in [4] were found to undergo high-temperature structural changes indicative of cation diffusion.

Oxygen ion conduction has been found comparatively recently in $\text{Ln}_{2+x}\text{Ti}_{2-x}\text{O}_{7-\delta}$ ($x = 0–0.286$, Ln = Dy–Lu) pyrochlore solid solutions, structurally related to the ZrO_2 –8 to 12 mol% Y_2O_3 and ZrO_2 –9 to 12 mol% Sc_2O_3 fluorites [9–12]. Subsequent work, concerned with not only titanates but also zirconates and hafnates, has focused on structural changes and ionic conduction in a variety of $\text{Ln}_{2+x}\text{M}_{2-x}\text{O}_{7-\delta}$ ($x = 0–0.286$; Ln = Sm–Lu; M = Ti, Zr, Hf) materials synthesized in a wide temperature range using chemical and mechanical homogenisation [9–15]. In the pyrochlore ceramics synthesis process precursors (co-precipitation and mechanical activation methods) were found to undergo low- and high-temperature phase transitions at 700–800 and 1300–1650 °C (depending on the system and composition), respectively, accompanied by changes in ordering. The high-temperature oxygen ion conduction in pyrochlores and pyrochlore-like solid solutions is due to the disordering transition at 1300–1650 °C, which results in a pyrochlore-like phase, PII, with both the anion and cation sublattices disordered [9–12]. Order-disorder phenomena in several rare-earth titanate pyrochlores $\text{Ln}_2\text{Ti}_2\text{O}_7$ (Ln = Gd, Y) and mixed $\text{Ln}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7$ (Ln = Dy, Gd, Y) were investigated in [16–22].

The nature of the low-temperature (700–800 °C) phase transition has not yet been studied in sufficient detail [23–25]. As shown previously at the study of $\text{Ln}_{2+x}\text{Ti}_{2-x}\text{O}_{7-\delta}$ (Ln = Er–Lu; $x = 0, 0.096$) phase formation process, the low-temperature transformation of the metastable disordered $\text{Ln}_{2+x}\text{Ti}_{2-x}\text{O}_{7-\delta}$ (Ln = Er–Lu; $x = 0, 0.096$) fluorite-like phase F^* or PI phase (cation-disordered pyrochlore) is

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accompanied by oxygen release and leads to the formation of an ordered pyrochlore (*P*) at 1100–1200 °C [24–26]. In studies of sol–gel derived $\text{Er}_2\text{Ti}_2\text{O}_7$ [25], the material prepared at 700 °C had a fluorite-like structure (*F*^{*}) and was deep pink. After firing at 800 °C, the material was almost colourless. The colour change was shown to be due primarily to the difference in covalency between the Er–O bonds (coordination number CN = 6) in the low-temperature fluorite phase (*F*^{*}) and those (CN = 8) in the defect pyrochlore (*PI*) obtained at 800 °C. Martos et al. [25] attributed the marked change in colour to both the *F*^{*}–*PI* phase transition and grain growth. Fuentes et al. [26] reported the mechanochemical synthesis and structural and microstructural characterization of $\text{Ln}_2\text{Ti}_2\text{O}_7$ (Ln = Y, Gd, Dy) with pyrochlore structure. The exothermic events observed in DTA have their origin in the ordering of the anion sublattice, whereas concerning the cation sublattice no evidence of cation ordering progress smoothly with temperature. So, the re-arrangement of oxygen sublattice only was observed at 800 °C in $\text{Ln}_2\text{Ti}_2\text{O}_7$ (Ln = Y, Gd, Dy) [26].

In this paper, we focus on the possible order-disorder phenomena in the $(\text{Dy}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_{7-\delta}$ ($x = 0, 0.1$) pyrochlore ceramics, what is important for potential practical application of these materials in the future. We obtained the temperatures of relaxation process and phase transition in these materials using temperature dependences of low-frequency dielectric permittivity and losses and Arrhenius plots of electrical conductivity for samples prepared using different methods (co-precipitation, mechanical activation and conventional solid-state reactions). Using TMA we present evidence of microstructural changes in these materials in the temperature range 700–800 °C.

2. Experimental

Polycrystalline samples for this investigation were prepared using co-precipitation, mechanical activation and solid-state reactions.

$\text{Dy}_2\text{Ti}_2\text{O}_7$ was prepared by solid-state reaction. A stoichiometric mixture of extra-pure-grade Dy_2O_3 and TiO_2 was ground and pressed at 20 MPa into discs, which were then fired in air at 1400 or 1600 °C for 4 h. $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ was synthesized from Dy_2O_3 , CaO and TiO_2 mechanically activated in an Aronov eccentric vibratory mill [27] under conditions described elsewhere [28]. After milling, the powders

were pressed at 20 MPa into discs 10 mm in diameter and 3 mm in thickness and heat-treated at 1400 °C for 4 h.

In addition, $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ was synthesized through hydroxide co-precipitation. An appropriate mixture of H_2TiCl_6 , LnCl_3 and $\text{Ca}(\text{NO}_3)_2$ solutions (the solution concentrations were determined gravimetrically) was added dropwise with vigorous stirring to a mixture of concentrated aqueous ammonia (50%), concentrated ammonium bicarbonate solution (25%) and water (25%). To prepare $\text{Dy}_2\text{Ti}_2\text{O}_7$, Dy(III) and Ti(IV) hydroxides (Dy : Ti atomic ratio of 1 : 1) were precipitated from chloride solutions by adding a mixture of the solutions to aqueous ammonia at pH 10.8. In both cases, the precipitate was washed with water (30 ml, four times) and then separated from the wash water by centrifugation. After drying at 100 °C for 24 h, the powder was ground and calcined at 650 °C for 2 h. Next, the powder was pressed at 10 MPa into discs 10 mm in diameter and 3 mm in thickness, which were sintered in air at 1400 or 1600 °C for 4 h and then furnace-cooled (cooling rate of 130 °C h⁻¹).

Structural changes were examined in ceramic samples $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$. In particular, the structure of $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ ceramics prepared using mechanical activation and high-temperature annealing at 1400 °C was studied by heat-treating the $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ pellets at 810 °C for 25 h and at 610 °C for 20 h and air-quenching them from each temperature in the liquid nitrogen. The quenched ceramics were characterized by x-ray diffraction (XRD) on a DRON-3 M diffractometer (CuK_α radiation, $2\theta = 15^\circ\text{--}65^\circ$). Another part of the $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ ceramics was ground in the powder and heat-treated at 810 and 610 °C for 25 hrs and air-quenched from each temperature. The defect structure of the samples was inferred from Rietveld analysis results (Co K_α radiation, $2\theta = 10\text{--}80^\circ$, step size of 0.05°, counting time of 3 s/step) [29].

$(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$ Ceramics samples were characterized by TG analysis in flowing helium (20 ml/min) during heating from 30 to 1000 °C at a rate of 10 °C/min using a SETARAM SETSYS Evolution 16/18 thermal analyzer in conjunction with a Pfeiffer OMNISTAR GSD 301 mass spectrometer. The TG module included an alumina tube mounted in a vertical tubular furnace. The carrier gas was introduced into the alumina tube from above, and a small part of the gas flow downstream of the sample was directed to the mass spectrometer through a stainless steel capillary. The time delay between thermal

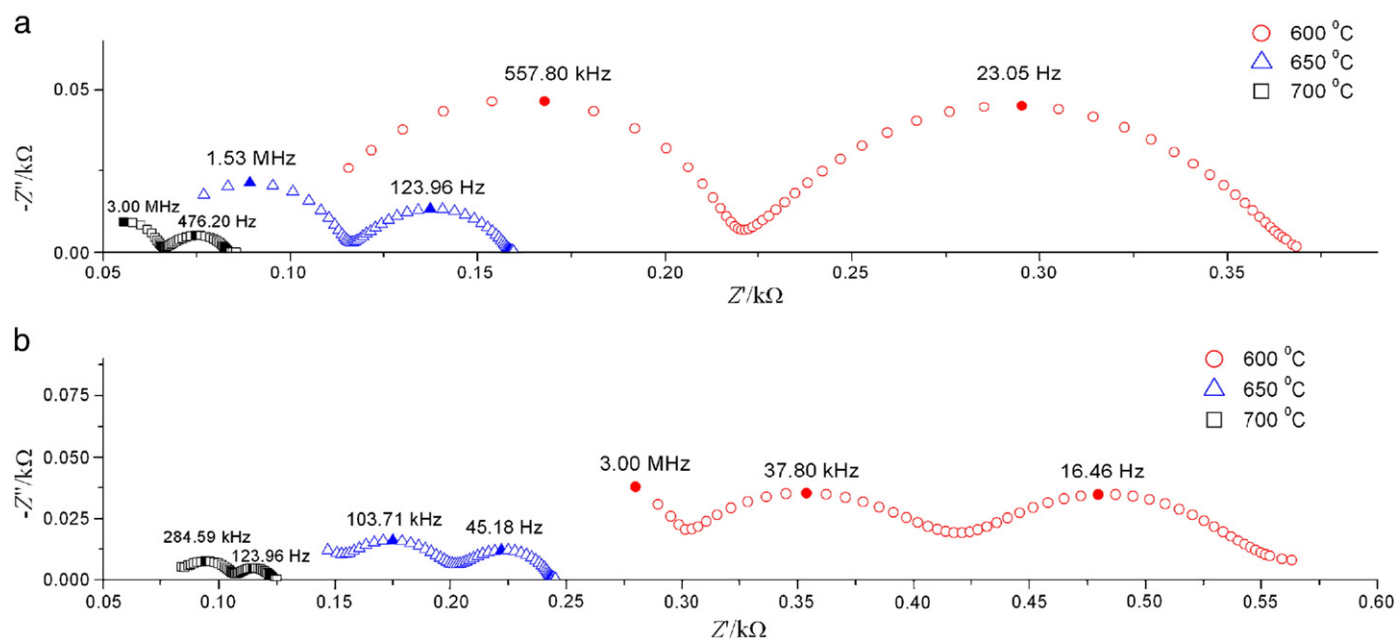


Fig. 1. Impedance spectra of (a) $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ (mechanical activation, sample A) and (b) $(\text{Dy}_{0.9}\text{Ca}_{0.1})_2\text{Ti}_2\text{O}_{6.9}$ (co-precipitation, sample B) in the range of temperatures 600–700 °C.

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